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Soil Acidification by Emitted Sulphur in the Athabasca Oil Sands Area

by

© Paul Y.P. Yeung

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
OF Master of Science

Department of Soil Science

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled Soil Acidification by Emitted Sulphur in the Athabasca Oil Sands Area submitted by Paul Y.P. Yeung in partial fulfilment of the requirements for the degree of Master of Science.

ABSTRACT

Field experiments were carried out in the Alberta Oil Sands Environmental Research Program study area to determine the amounts of sulphur emission absorbed by a lichen-covered soil. The soil held in containers was set out at four sites, two downwind from the Great Canadian Oil Sands plant and the other two remote from the plant. In a laboratory experiment, a similar soil was exposed to an atmosphere of controlled SO2 concentration. In both the field and laboratory, the soil increased significantly in sulphur content on exposure to SO2. There was a decrease in soil pH and an increase in sulphur content mainly in the surface layers of the soil. Much of the absorbed sulphur gained by the soil was found in non-sulphate form.

Rainfall collected at the three sites in the AOSERP study area during the experimental period was slightly acid. The amount of sulphur brought down in rain was very small when compared with the amount of sulphur absorbed directly from the atmosphere by soil. Direct absorption by soil apparently is the most important mechanism by which emitted SO2 is deposited in Alberta.

Field experiments were also carried out to determine the rate of sulphate-sulphur movement and soil acidification on application of elemental sulphur and sulphuric acid and the rate of correcting soil acidity after liming. The top-dressing of K2SO4 on the three forest soils indicated

that sulphate moved quickly down into the soil profiles in just a few summer months but only a minority of the applied sulphate was recovered by 0.1M CaCl2 extraction. These results indicate that the depositions of emitted sulphur on forest soil may be mostly missed by determination of only soluble sulphate-sulphur in the soils. Applied elemental sulphur caused soil acidification mainly in the upper layers of soils, but not all of the elemental sulphur was oxidized twelve months after application. Applied sulphuric acid moved quite rapidly down soil profiles and at the same time lowered soil pH. Broadcast limestone was slow in mobility and only the soil surface was neutralized in a period of twelve months.

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1. INTRODUCTION

As a result of increasing industrialization and energy consumption, the amount of waste substances emitted into the air has also increased. These atmospheric pollutants and especially sulphur dioxide (SO2) have created environmental problems with human health, animals, vegetation, water and soils. In Alberta, sulphur emissions are mainly located at gas processing plants. This study mainly concerns the Athabasca Oil Sands area which is part of the boreal forest region of northeastern Alberta. It has been estimated that about a quarter million tonnes of SO2-sulphur are emitted into the air each year in Alberta from processing natural gas and oil sand extraction (Tollefsen, 1972).

In this work, a field experiment was conducted from May, 1976 until June, 1977 to study the impact of SO2 gas on soils. At the time of this study, the only SO2 emitting source in the Oil Sands was the Great Canadian Oil Sands plant. The plant started to produce oil in September, 1967 producing an average of 60,000 barrels of oil per day (Information about the Athabasca Tar Sands of Alberta, Syncrude Canada Ltd., 1976). The Syncrude plant did not start oil mining until 1978. Even with advanced technology to reduce air pollutants, the emission of SO2 is almost unavoidable during oil extraction. The Alberta government would allow a maximum of 287 long tons of SO2 to be emitted a day by the Syncrude plant alone (Syncrude: Environment,

vol. IV No.1, 1976).

Sulphur dioxide emissions may affect a large area because the SO2 may remain in the air for a period of two to four days and thus may travel a long distance from the emission source before it is deposited onto the ground. Swedish scientists believed that about half of the sulphur deposited in Sweden originated from neighbouring countries (Anon., 1972). Only a small percentage of the emitted SO2 may be returned in the vicinity of the emission source. Mohtadi (1975) estimated only a few per cent of the SO2 emitted fell directly to the ground within a thousand square miles surrounding sour gas plants in Alberta. The rest was either deposited on the ground by rain and snow or dispersed in the atmosphere. Other work in Alberta, with soils placed at varying distances from SO2 emitters, indicated that SO2 absorption by soils was more important near emitters (Nyborg et al., 1977; Hua Hsu and Hodgson, 1977; and Nyborg and Walker, 1977). The sulphur dioxide and other forms of sulphur gas in the atmosphere are oxidized to sulphuric acid which may be held in droplets of water. This acid can be neutralized by acid-neutralizing particulates such as oxides of Ca, Mg and K in the air. However, if the deposits are acid-forming, there will be an excess of acid in the air or acid rain.

Sulphur dioxide emissions cause soil acidification slowly. Nyborg et al. (1977) estimated that as a result of SO2 emissions, soils are acidified at a rate of

approximately one pH unit in 20 years in the vicinity of SO2 emitters. About 17 per cent of the agricultural soils in Alberta are naturally acidic (pH 6.0 or less) (Nyborg and Walker, 1977), and a further drop in soil pH due to increased acidity means the yield of some acid sensitive crops would be decreased. Most of the forest soils in the area of this study are also naturally acidic (pH about 5.5) and further lowering of soil pH as a result of continuous SO2 emissions could be critical to natural vegetation ground cover.

This thesis is concerned essentially with measuring the amount of emitted sulphur taken up by soils as opposed to the sulphur deposited by rain, and with determining changes in soil pH and soil sulphur content after exposure of SO2 emission.

The major components of the objective of this study are:

1. to determine the amounts of SO2 taken up by lichen-covered soils, both in natural and controlled conditions.
2. to determine the fate of SO2 absorbed by lichens and soils.
3. to measure the rate of downward movement of sulphate-sulphur in soils with applied K2SO4.
4. to study the effects of soil acidification by applied elemental sulphur and sulphuric acid.
5. to study the application of calcium carbonate as a

counter measure against soil acidification of forest soils.

2. LITERATURE REVIEW

2.1 Nature of Sulphur in Soils

Sulphur occurs in soil in both inorganic and organic forms. Inorganic sulphur includes soluble and adsorbed sulphate as well as compounds of lower oxidation state such as sulphide, polysulphide, sulphite, thiosulphate and elemental sulphur (Williams, 1975). However, most of the inorganic sulphur in soils is usually found as adsorbed or as easily-soluble sulphate used by plants.

The amount of inorganic sulphur may vary from region to region of the world. In temperate regions, inorganic sulphur only accounts for a small percentage of the total sulphur in soils. Most of the sulphur is held in the organic matter. Bettany _et al_. (1973) found that inorganic sulphur ranged from 0.5 to 13.5 ppm which was only 0.5 to 3.6% Of the total sulphur in some Saskatchewan soils. But Neptune _et al_. (1975) reported that some Brazilian soils of subtropical regions contain adsorbed inorganic sulphur from 5 to 23% of the total sulphur.

Inorganic sulphur normally occurs as sulphate in well-drained soils and the amount of reduced sulphur compounds account for less than 1 ppm (Freney, 1961). But in waterlogged soils, large amounts of sulphides and even elemental sulphur could be found (Fleming and Alexander, 1961). Inorganic sulphur may also occur as gypsum ($CaSO4.5H2O$) in calcareous soils or as sodium sulphate in

saline soils (Nyborg, 1978). The presence of gypsum or sodium sulphate may account for a large percentage of the total sulphur in soil.

The total sulphur contained in organic matter in soils ranges from about 0.005 to 0.05 per cent (Nyborg, 1978). Even though organic sulphur represents the majority of the total sulphur in most soil, its chemical nature is not completely known. Determinations of sulphur in soil are often confined to only total sulphur and sulphate-sulphur. However, Williams (1975) divided organic sulphur into three broad groups as follows: hydriodic acid-reducible sulphur, carbon-bonded sulphur and Raney-nickel-reducible sulphur. The percentage of hydriodic acid-reducible sulphur ranged from 30 to 70 percent of the total organic sulphur. Carbon-bonded sulphur comprises about 50 per cent of the total organic sulphur. The amount of Raney-nickel-reducible sulphur (which is a subfraction of the carbon-bonded sulphur) varies from soil to soil but on the average it represents less than 30 percent of the total organic sulphur in soil.

The amounts of total sulphur (S), total nitrogen (N), and total carbon (C) are apparently related in soils. Even though the amounts of S, N and C may vary considerably within one soil zone, Bettany et al. (1973) found that of the 54 soils collected from five zones in Saskatchewan, the mean C:S, N:S ratios were quite similar.

Soil sulphur is mineralized and immobilized in soil by

soil microorganisms (Alexander, 1961). About 1 to 3% of the organic sulphur is converted into inorganic sulphur and about the same amount is converted back to the organic fraction each year (Nyborg, 1978). According to Freney et al., (1962) the amount of sulphur mineralized depends largely on the N:S of the freshly added organic matter but not on the rather stable N:S of the soil organic matter.

2.1.1 Oxidation of Elemental Sulphur

"Approximately five million tons of elemental sulphur are produced annually in Alberta from processing of sour natural gas" (Nyborg, 1974). Elemental sulphur can be used to reduce soil alkalinity and as a source of sulphur to plants where soils are deficient in sulphur. However, accidental spilling or windblown sulphur dust from stockpiles onto adjacent lands and waters can cause severe damage due to acidification.

Elemental sulphur is produced at almost all the large gas processing plants in Alberta when H2S is scrubbed from sour natural gas and converted to elemental sulphur, the form used for storage and transportation. It is not economical to convert the last few per cent of the H2S into elemental sulphur, therefore, the remainder is given off as SO2.

The crude oil, which is now being produced by G.C.O.S. and Syncrude, is extracted from oil sand which contains about 4.5% sulphur and consequently the process generates

elemental sulphur as well as SO2.

The wind erosion of elemental sulphur from storage piles and the handling the elemental sulphur, may result in the deposition of sulphur dust within 2 or 3 km of the source. Depending on the rate of deposition, and on other factors, soils and waters may quickly become very acid as the deposited elemental sulphur becomes sulphuric acid.

Elemental sulphur, sulphides and several other inorganic sulphur compounds can be oxidized in soil by purely chemical processes, but these are usually much slower and therefore of less importance than oxidation involving microorganisms (Weir, 1975). There are a number of organisms capable of oxidizing elemental sulphur. They include heterotrophs, photo-autotrophs, and chemo-autotrophs. The best known and usually considered to be the mose important group of sulphur oxidizing microorganisms are the autotrophic bacteria belonging to the genus Thiobacillus. Some of the better know species are *T. thiooxidans*, *T. thioparus*, *T. denitrificans* and *T. ferrooxidans*. They are obligate autotrophs which use CO2 as their carbon source. Thiobacilli are not found in abundance in soil probably due to the fact that sulphur compounds which are their energy source do not normally accumulate in soils (Starkey, 1965). A few species are facultative autotrophs which are able to use either oxidizable sulphur or organic substances as their energy source. Most Thiobacilli are strictly aerobic but *T. denitrificans* is a facultative aerobe which uses nitrate

under anaerobic conditions as an electron acceptor in place of oxygen. Among the species, *T. thiooxidans* and *T. ferrooxidans* are the most acid tolerant and are found where there is a good supply of elemental sulphur. They grow best at pH 2.0 - 3.0 and can produce 1.0M sulphuric acid (Starkey, 1965).

The oxidation of elemental sulphur to sulphate proposed by Peck (1960) involves intermediate products such as thiosulphate (S2O3=), tetrathionate (S4O6=), trithionate (S3O6=) and sulphite (SO3=). The oxidation reaction is mostly a biological process and and the rate of the process is affected by several factors outlined by Weir (1975): (a) the substrate, the rate and placement of sulphur; (b) the microbial population; and (c) the soil, its temperature, moisture and aeration, type and properties and nutrient supply. As outlined by Tisdale and Nelson (1975), oxidation of elemental sulphur goes most quickly when it is very fine in particle size, when soil moisture is near field capacity, and when soil temperature is near 30°C. It would seem that most natural soils contain elemental sulphur oxidizing bacteria, but after the treatment of soils with elemental sulphur the number of the bacteria increases greatly. A demonstration of quick conversion from elemental sulphur to sulphuric acid was given by Bertrand (1973). When elemental sulphur of very fine particle size was added to a soil, which had received elemental sulphur before, the soil oxidized 6,100 ppm of sulphur in 21 days at 22°C.

2.2 SO2, Its Impact on Soils

Soil and plant are interrelated in the forest ecosystem. Any change in chemical, biological or physical properties of soil may mean a change in its vegetative cover. Any change in vegetative cover will result in changes in soil properties. Increasing emissions of anthropogenic SO2 into the atmosphere have resulted in growing concern on the probable changes to soil and plant.

Small quantities of sulphur oxides are normally present in the atmosphere from biological oxidation of sulphides, but in addition SO2 is emitted into the atmosphere from the burning of fossil fuels which contain sulphur. The ways by which SO2 is returned to earth include: neutral sulphates and sulphuric acid formed in the air, which are carried down by rain or snow; SO2 intercepted by vegetation and then washed off by rain; the settling out of dry particles, composed of various salts, from the air; and direct absorption by soil. The first and second processes are referred to as wet deposition and the third and fourth processes as dry deposition. Dry deposition is considered to be the most important mechanism. Whether SO2 deposition is wet or dry, usually the ultimate result is soil acidification. However, the degree of soil acidification depends greatly on the properties of soils (Nyborg, 1978). Soils with free CaCO3 (calcareous soils) are unlikely to be acidified since sulphate reacts with calcium to form a neutral salt (CaSO4). But most soils are not calcareous and

these soils can be acidified slowly due to continuous SO2 emissions. Soils have great capacity to sorb SO2 gas (Smith *et al.*, 1973; Bremner and Barnwart, 1976). When a soil was set out in containers protected from rain at six sites in Central Alberta for eight weeks, the soil at the four sites 6 to 15 km from SO2 emitters gained 41 ppm of total sulphur although only two ppm of the sulphur appeared as sulphate-sulphur (Hua Hsu and Hodgson, 1977). Cox (1975) set out three soils for 19 weeks in a similar experiment and found that pH of the soils was depressed at 15 to 25 km from the source of emission, accompanied by increased sulphate-sulphur. A laboratory experiment with treatment of the soils with low concentration of SO2 (30 ppb) in the air for 48 hours, resulted in small but significant decreases in soil pH. The amount of sulphur absorbed by soils (up to 50 KgS/ha) is far greater than that absorbed by water surfaces (4 to 15 KgS/ha) and brought down by rainfall (up to 4 KgS/ha) annually in Alberta (Nyborg *et al.*, 1977). Snow contributes less than 1 kgS/ha annually.

In Alberta, rain and snow have little sulphur and are seldom acid (Nyborg and Walker, 1977) but in heavily industrialized areas, precipitation with pH ranges from 4 to 5 represents a possible threat for forest and fresh-water ecosystems (Abrahamsen *et al.*, 1975). Although the effects of acid precipitation on soil properties are very complex, its common effects are pH depression, increase in sulphur content and leaching of nutrient minerals. Abrahamsen *et al.*

(1975) studied the effects of acid rain on soil chemistry. They found that artificial rain of pH 3 or lower could significantly reduce base saturation of soil. Acid rain could increase leaching of Ca and Mg. Acid rain also inhibited the rate of nitrification (Hovland and Ishac, 1975). No nitrification occurred in humus from unlimed plots acidified by acid rain. However, liming could restore the normal rate of nitrification.

2.3 The Fate of SO2 in the Atmosphere

Sulphur exists in the air as sulphur dioxide (SO2), hydrogen sulphide (H2S), sulphuric acid (H2SO4) and sulphate salts. As stated by Overrein (1977) "Sulphur compounds are introduced into the atmosphere by three main processes: H2S from biological decay, SO4 from sea salt, and SO2 from anthropogenic sources. The main anthropogenic sources are the burning of sulfur-containing fossil fuels and smelting of sulfide ores." He also pointed out that natural sources of sulphur emissions are slightly more important than anthropogenic emissions on a global scale. But in a heavily industrialized area such as in Europe, natural emissions are only 10% of anthropogenic emissions (25×10^6 tons sulphur per year). The reaction of SO2 in the atmosphere is undoubtedly complex and dependent on many factors such as humidity, sunlight and the presence of catalysts.

Sulpur dioxide in the air undergoes both photochemical and catalytic reactions in the air (Mohtadi and Gyuse,

1975). Photochemical reaction of SO_2 is a relatively slow process which involves oxygen in the air and ultraviolet solar radiation. Sulphur dioxide is photo-oxidized slowly to produce sulphur trioxide as follow:

$$2SO_2 + O_2 \xrightarrow{hv} 2SO_3$$

Sulphur trioxide then reacts with water to form sulphuric acid. Catalytic reaction of SO_2 in the air is considered to be the most important and rapid chemical reaction as SO_2 is transformed into sulphate particulates in the presence of water droplets, clouds and fog. The reaction is catalyzed by transition metal ions or dust particles and ammonia in the air.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \longrightarrow H_2SO_4$$

The sulphurous acid is rapidly oxidized to sulphuric acid by dissolved oxygen in the water. In industrial areas, transition ions such as iron which is the most abundant occur as impurities in the air. Among the other metal salts which also catalyze the reaction, $MnSO_4$ is the most efective (Mohtadi and Gyuse, 1975).

Sulphur dioxide that is not transformed will travel in the air depending on prevailing wind until it is brought down by rain or snow. Some of it will be adsorbed onto

surfaces of vegetation and ground.

2.4 Soils as a SO2 Sink

Soil is an important natural sink for gaseous atmospheric pollutants because it is capable of absorbing large amounts of SO2 and other atmospheric pollutants (Alway et al., 1937; Fuhr et al., 1948; Terraglio and Manganelli, 1966; Abeles, 1971; Smith et al., 1973; Ghiorse and Alexander, 1976).

As early as 1937, Alway et al. found SO2 absorption by soils exposed to SO2 source for a month.

Fuhr et al. (1948) found that 5 to 10 ppm of SO2 in the air was absorbed completely by 13 ft^2 of soil containing 11% moisture in only 40 minutes.

Terraglio and Manganelli (1966) exposed two soils (a very acidic sandy soil and a less acidic sandy loam) to various concentrations of SO2 and found that an increase in soil moisture content increased SO2 absorption. Nakayama and Scott (1962) described soil moisture content as an important factor in determining the amount of SO2 absorption because more water would dissolve more SO2. Terraglio and Manganelli (1966) also found that no SO2 was absorbed by a dry acid soil but a less acid soil retained significant amounts of SO2.

Smith et al. (1973) used gas chromatographic studies to show that soils have the capacity to absorb substantial amounts of SO2 and other gases. They also found that

increase in soil moisture could increase SO2 absorption by soils, however, the rate and amount of absorption were not significantly correlated with soil pH, organic matter content and clay content. They also showed that soil microorganisms were not responsible for absorption of gases, although Abeles _et al_. (1971) found that microorganisms may play a role in absorption of SO2.

Ghiorse and Alexander (1976) found that SO2, when adsorbed on a soil, had gone through the conversion to sulphite and then to sulphate within 10 hours, even when the soil has been irradiated. That is, this conversion was apparently not biological. They also found that a portion of the sulphur gained by the soil was not extractable. Nyborg _et al_. (1977) showed that when two soils, one Chernozemic and one Luvisolic, were exposed to an atmosphere containing 24 ppb of SO2 for 30 days, the soils gained 18 and 16 ppm of sulphur. Only one-half of this sulphur was extractable in water.

All this evidence showed that soils have the capacity to quickly absorb substantial amounts of SO2. Further, the absorbed SO2 is converted to sulphuric acid, and some of the gained sulphur is not found again as soluble sulphate.

2.5 Movement of Inorganic Soil Sulphur

Apparently, much of the SO2 emissions are deposited on the soil as sulphates. It is, therefore, important to understand their subsequent movement in the soil.

Sulphur in the form of sulphate ions is known to be weakly or moderately retained by soils. Harward and Reisenauer (1966) stated that "although SO4= may account for less than 10 percent of the total sulphur in surface soils, the amounts in subsoils may represent a significant portion of the total". The extent of leaching or movement of sulphate ions depends on various soil characteristics. As a result of some lysimeters studies, Stauffer and Rust (1954) showed that a significant amount of sulphur in soils was lost by sulphate leaching. An average of 33.3 kgS/ha was lost annually by leaching in eight Illinois soils. Chao _et al_. (1962b) used soil columns to study the movement of S^{35} tagged-sulphate applied as gypsum. Using different rates of application of water, the distribution of the surface-applied sulphate showed a well-defined pattern of gradual downward movement. Also, a higher rate of sulphate application resulted in a greater amount of sulphate downward movement.

Some factors affecting sulphate retention by soils are:

1. Types of clay minerals.

   It has been established that kaolin minerals adsorb more sulphate than montmorillonoids (Chao _et_ _al_., 1962c). This involves the exchange of SO4= for OH^- on the edges of silicate clays. Harward and Reisenauer (1966) reported that "the greater retention of sulphate by kaolinite than by montmorillonite has been attributed to a higher proportion of anion-exchange sites on 1:1

type clays, and higher negative charge with associated anion repulsion on 2:1 type clays". Kamprath _et_ _al_. (1956) also reported the same result in their experiment. The 1:1 type of clay minerals adsorbed more sulphate than 2:1 type clay minerals because of a high content of free iron and aluminum oxides.

2. Effects of aluminum and iron oxides.

Free aluminum and iron oxides show a marked tendency to retain sulphate. Chao _et_ _al_. (1962c) showed that "dealuminated" and "iron-removed" soils absorbed much smaller amounts of sulphate than did the untreated soils. They also reported iron oxides might be more important in sulphate adsorption than aluminum oxides.

3. pH.

Sulphate adsorption increases with decrease in soil pH. Kamprath _et_ _al_. (1956) found such a relationship between sulphate adsorption and soil pH was true for all sulphate concentrations studied. There is little sulphate retention when soil pH is above 6.0. Liu and Thomas (1961) applied K2SO4 onto an acid soil and found that the amount of sulphate retained increased with time. Also, sulphate retention increased as the pH was lowered and the salt concentration was increased. Under both of these conditions, hydroxyl ions would be replaced more easily by sulphate ions. Harward and

Reisenauer (1966) reported that the zero point of charge (ZPC)* must be considered when determining the effect of pH on sulphate adsorption.Taking alumina oxide as an example, it involves a charge transfer across the alumina-water interface as pH changes. As pH increases, the negative charge on the complex increases. On the other hand, when pH decreases, the plus charge on the complex increases and more sulphate will be adsorbed.

4. Sulphate concentration.

The amount of sulphate adsorbed by a soil increases with increasing concentration of sulphate in solution but Kamprath _et al_. (1956) stated that "at higher concentrations, however, a smaller percentage of the added sulfate will be adsorbed". In their sulphate adsorption-desorption studies, Chao _et al_. (1962a) also found that sulphate retention is dependent on sulphate concentration of the equilibrium solution.

5. Effects of anions.

Harward and Reisenauer (1966) stated that "there are marked differences in the retention of different anions and on the effects of other anions upon sulfate. Sulfate is generally considered to be weakly held with the strength of retention in the order of phosphate > sulfate > nitrate = chloride". Chao (1964) reported that inorganic anions such as phosphate, molybdate and

---

*ZPC is the pH at which silicate surfaces are electrically neutral.

fluoride in that order were most effective in depressing sulfate retention. Kamprath _et al_. (1956) found sulphate retention was reduced as phosphate ions in solution increased, however, no explanation was given as to why soils and clay minerals studied had a greater affinity for phosphate than for sulphate.

6. Effects of cations.

In their paper, Chao _et al_. (1963) stated that "the magnitude of sulfate adsorption by soils saturated with different cations followed the order of chemical valency of the saturating cation ($Al^{3+} > Ca^{2+} > K^{+}$). Saturation with tri- or divalent cations resulted in greater sulfate adsorption than with monovalent cations. The influence of different cations on sulfate adsorption was shown to be associated with two factors: nature of the cations and pH while pH had greater influence than the type of cations".

7. Liming.

Application of lime generally increases the movement of sulphate through soil columns (Chao _et al_., 1962b; MacIntire _et al_., 1941; Ensminger, 1954), however the mechanism or reaction of liming was not discussed. This reaction is probably related to increased soil pH since very little sulphate will be retained in the surface soil when limed to pH 6.0 or higher (Kamprath _et al_., 1956).

8. Organic matter.

   With organic matter removed, the amount of sulphate adsorbed in a soil decreased (Chao *et al.*, 1962c). The authors believed it to be a qualitative rather than a quantitative factor.

9. Texture and permeability of soil.

   Texture and permeability of a soil should have effects on sulphate retention, however, Chao *et al.* (1962b) did not think that this was always a determining factor.

10. Time.

    The amounts of cations and anions adsorped by a soil are time dependent. In their equilibrium experiment, Chang and Thomas (1963) found that "the quantity of anions held by a Cecil subsoil increases with time".

3. EXPERIMENTAL PROCEDURES

3.1 Descriptions of the Study Area

The Athabasca Oil Sands area is located in the boreal forest region of northeastern Alberta. The field plots are located at three locations (Figure 1):

(1) AOSERP Camp site

(2) Ruth Lake

(3) Thickwood Hills

Field stations for SO2 uptake experiment are located both south and northeast of the SO2 emission source (Figure 2). When this study was conducted, the only sources of SO2 emissions in the study area were located at the Great Canadian Oil Sands processing plant located at Tar Island about 70 km north of the town of Fort McMurray. The Syncrude Plant which is 40 km north of Fort McMurray began production of synthetic crude oil late in 1978.

3.1.1 AOSERP Camp site

This site is located 11 km northwest of the emission source on well-drained aeolian sand. The principal tree species is jack pine (*Pinus banksiana*) with a sparse understory of bearberry (*Arctostaphylos uva-ursi*), bog cranberry (*Vaccinium vitis-idaea*), and blueberry (*Vaccinium myrtilloides*). There is also a nearly continuous lichen stratum principally of *Cladina mitis* and *C. arbuscula*.

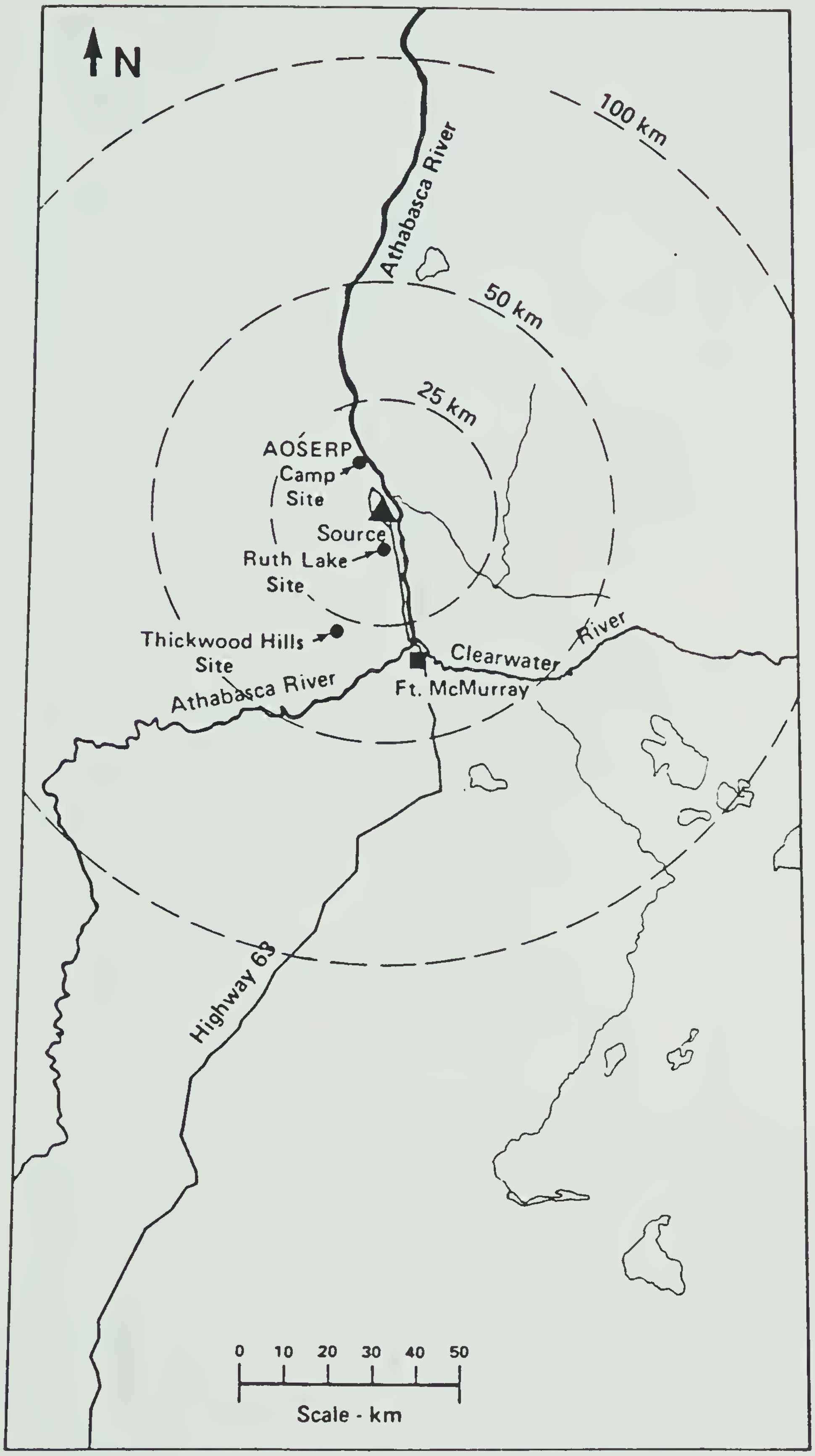


Figure 1. Location of three sites where experimental plots were laid out on undisturbed forest soils. The plots were used for determining the effect of applied elemental sulphur, sulphuric acid and lime on soil acidity, and for measuring the rate of movement of applied sulphate sulphur in forest soils.

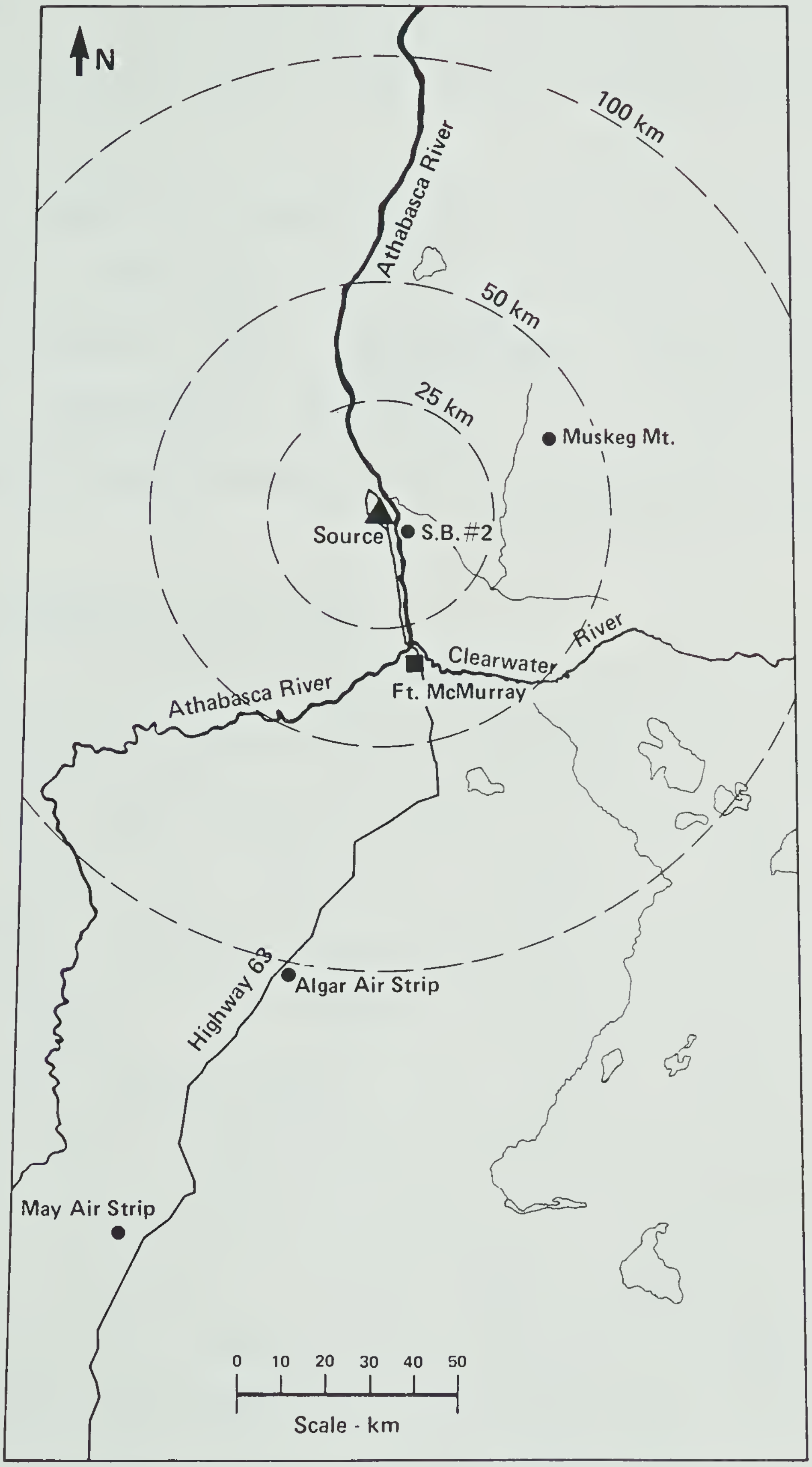


Fig. 2 Location of 4 stations with lichens and soils exposed to SO_2 emission

3.1.2 Ruth Lake site

This site is located 6 km south of the emission source on poorly drained aeolian sand with a water table situated less than one meter from the surface during the summer months.

The vegetation consists of scattered individuals of jack pine seedlings with a low shrub stratum comprised mainly of leather leaf (*Chamaedaphne calyculata*) and bog rosemary (*Andromeda polifolia*). The bryophyte stratum is diverse but consists mainly of *Polytrichum strictum*.

3.1.3 Thickwood Hills site

This is a well-drained upland site on glacial till located approximately 27 km southwest of the emission source. The tree species present are large jack pine in a dense stand of smaller trembling aspen (*Populus tremuloides*). There is also a few small white spruce tree (*Picea glauca*). The sparse tall shrub stratum consists of green alder (*Alnus crispa*). The lichen stratum is almost continuous and is comprised principally of *Cladina mitis*.

Soil profile descriptions at the three sites are given in Appendix Tables 1, 2, and 3. The texture and bulk density of the soils at these sites are given in Appendix Table 4. The soils at the AOSERP Camp site and Ruth Lake site are sandy while the soil at Thickwood Hills is a clay loam texture.

3.1.4 SO2 Monitoring Stations

Soils covered with lichen were placed under rain shelters at the four SO2 monitoring stations located south and northeast of the SO2 emission source (Figure 2). Rain shelters were built to prevent animals and birds from disturbing the samples. The distance and direction of each station in relation to SO2 emission source are as follows:

(1) Steepbank #2, 4 km ESE

(2) Muskeg Mountain, 38 km ENE

(3) Algar, 101 Km SSW and

(4) May, 173 Km SW.

3.2 Experimental Plot Layouts and Treatments

The experimental plot layouts are given in Figures 3 to 6. The two experiments are:

(1) Downward movement of sulphate-sulphur experiment.

(2) Soil acidification and liming experiment.

Each site location was selected on level ground with the AOSERP Camp site, on gently rolling topography. Each treatment was located three meters away from each other to eliminate contamination from lateral movement of applied chemicals. Replicates of treatments in the Thickwood Hills site are scattered because of the dense trees but treatments of each replicate were close enough together to minimize variation in soil properties. The treatments of downward movement of sulphate-sulphur are given in Figure 3 and the treatments of soil acidification and liming experiment are

T1 = Nil
T2 = 56 kg S as K_2SO_4/ha
T3 = 112 kg S as K_2SO_4/ha

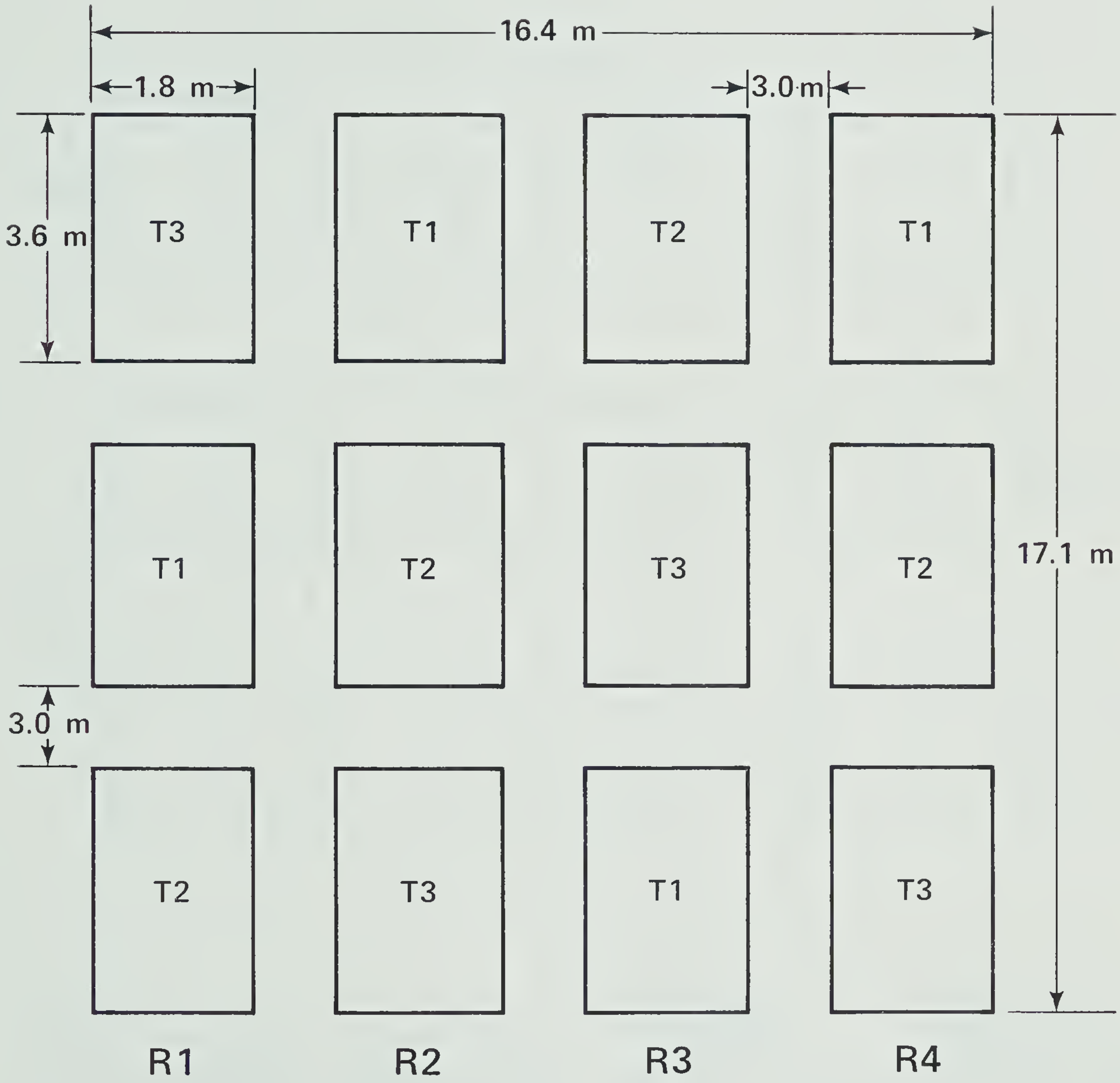
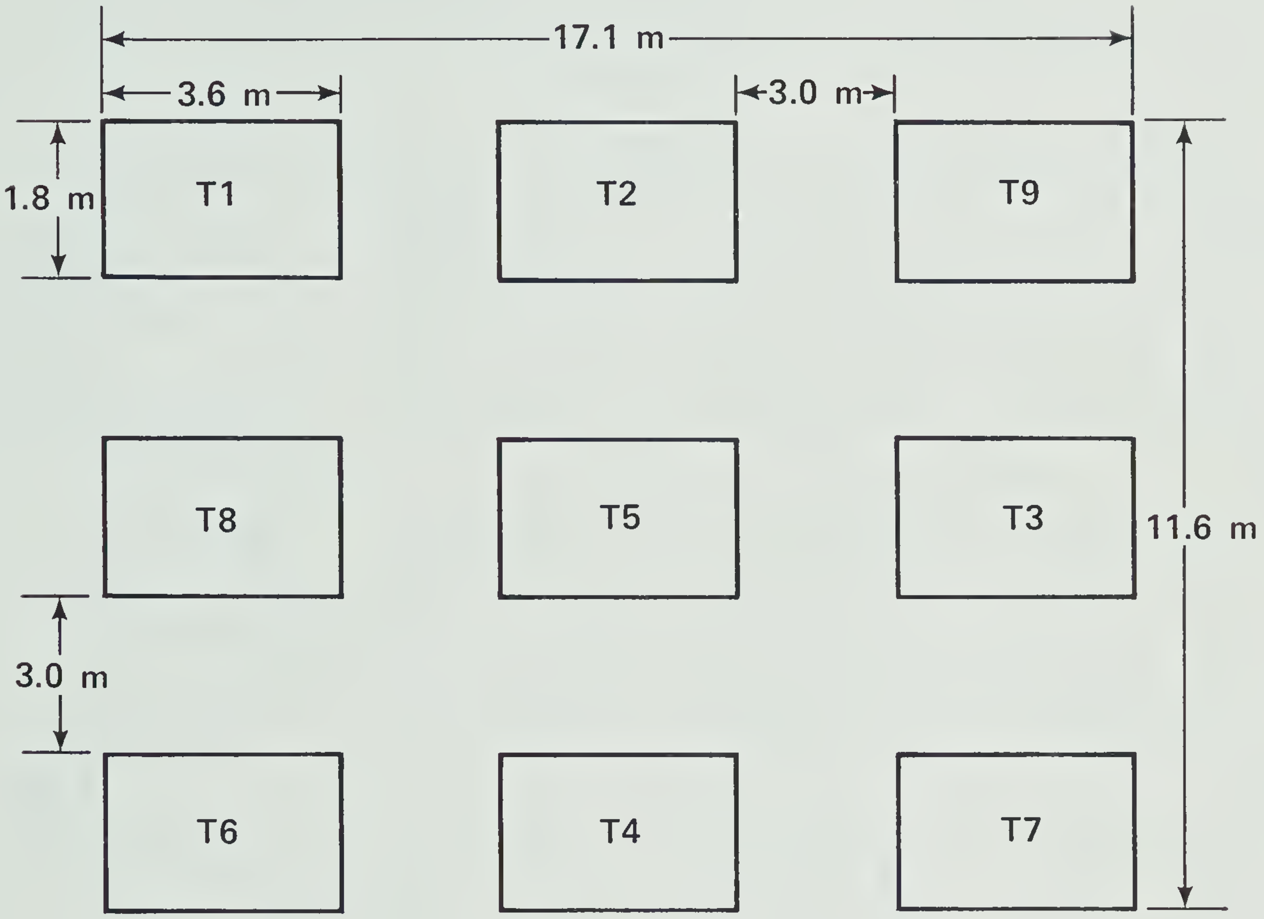


Fig. 3 Plot layout at AOSERP Camp Site
(Downward movement of SO_4-S Experiment)

2) Soil acidification and liming experiment — one of the replicates.



T1 = Nil
T2 = S° + inoculant @ 56 kg S/ha
T3 = S° + inoculant @ 280 kg S/ha
T4 = S° + inoculant @ 560 kg S/ha
T5 = H_2SO_4 @ 56 kg S/ha
T6 = H_2SO_4 @ 280 kg S/ha
T7 = H_2SO_4 @ 560 kg S/ha
T8 = lime @ 2500 kg S/ha
T9 = lime @ 2500 kg/ha + 280 kg S°/ha + inoculant

Fig. 4 Plot layout at AOSERP Camp Site (Soil acidification and liming experiment)

1) Downward movement of SO_4-S Experiment
Plot plan is the same as in AOSERP camp site.

2) Soil acidification and liming experiment

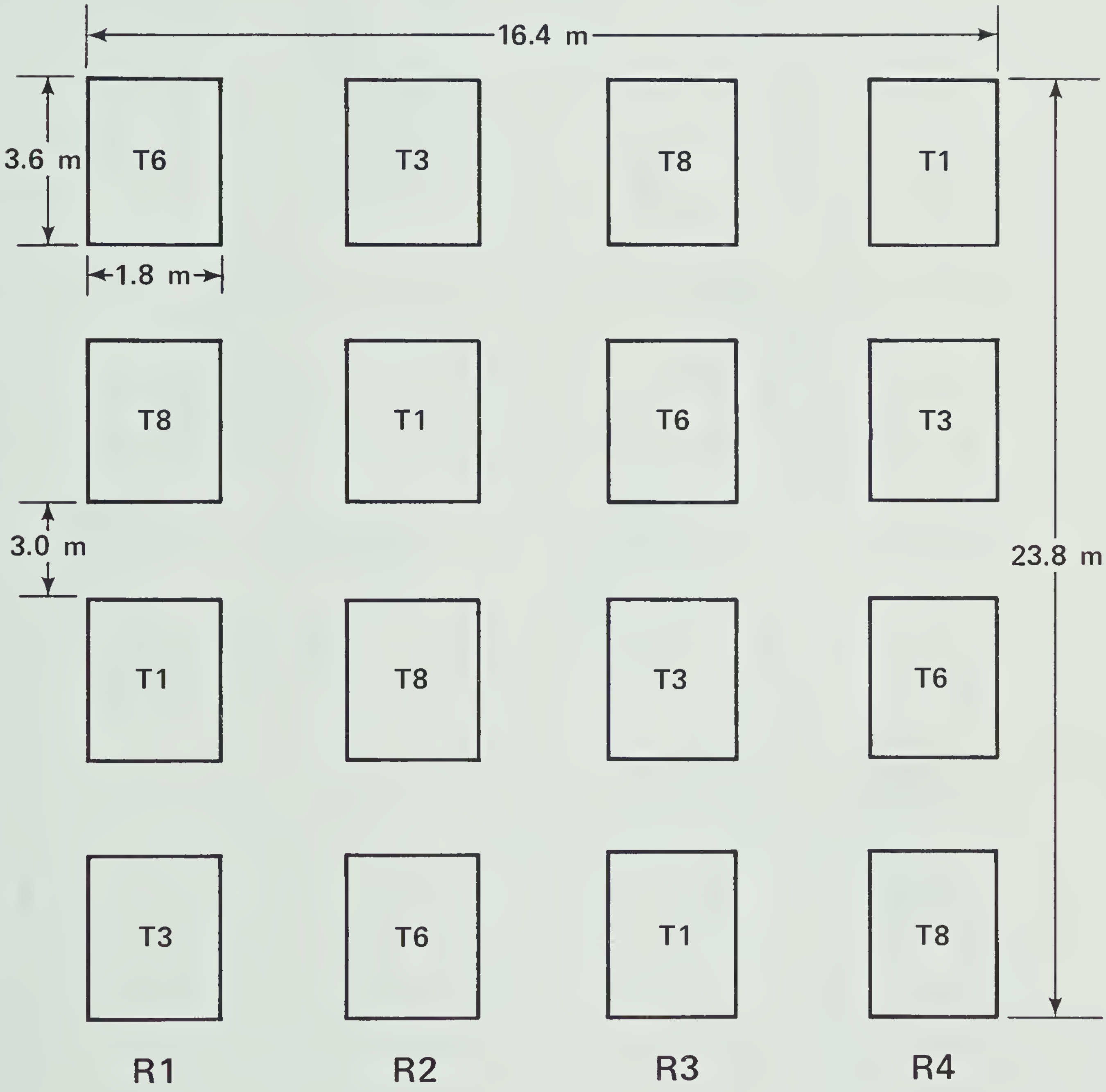


Fig. 5 Plot layout at Ruth Lake site

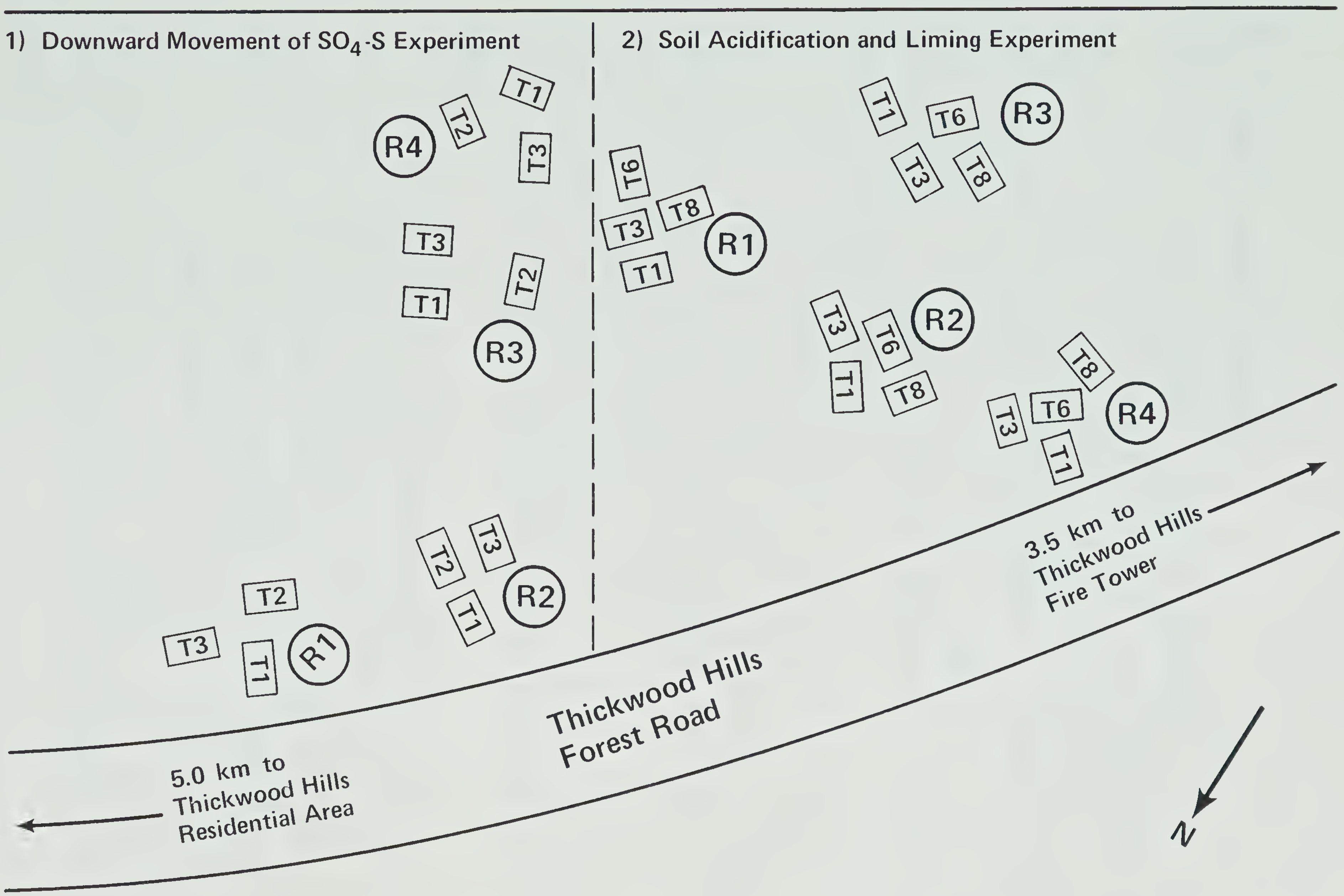


Fig. 6 Plot layout at Thickwood Hills site.

given in Table 1.

3.3 Sampling and Analyses

3.3.1 Rate of SO2 Uptake (Field Experiment)

The soil samples used for this experiment were obtained from an area 170 km south of the SO2 emission source. The samples were removed from the ground in such a manner that the lichen layer on the soil sample surface remained undisturbed. A description of a typical soil sample used is given in Appendix Table 5.

The intact soil samples were placed in plastic pots of 16.5 cm inside diameter and 13.0 cm in height. Six replicates of each were set out under rain shelters at the four SO2 monitoring stations from May to October, 1977. Every month the soil samples were brought to pre-determined field capacity moisture content by the addition of distilled water.

At the end of the exposure period the pots were sealed in plastic bags and returned to the laboratory for chemical analyses. The lichen material, the organic layer (LFH) and mineral soil (Ae) were separated, dried, ground and analyzed for pH, sulphate-sulphur and total sulphur. Results were expressed on an area basis (kg/ha) by multiplying the results in ug/g soil by the soil bulk density and exposed surface area.

Table 1. Rates of elemental sulphur, sulphuric acid and lime applied of the soil acidification and liming experiment.

Treatment No.	Treatment Description
1	Control
2	Elemental sulphur at 56 kg S/ha + inoculant
3	Elemental sulphur at 280 kg S/ha + inoculant
4	Elemental sulphur at 560 kg S/ha + inoculant
5	0.1 N H_2SO_4 at 56 kg S/ha
6	0.5 N H_2SO_4 at 280 kg S/ha
7	0.5 N H_2SO_4 at 560 kg S/ha
8	Lime at 2500 kg/ha
9	Lime at 2500 kg/ha + elemental sulphur at 280 kg S/ha + inoculant

Notes: Elemental sulphur was very fine (100 mesh) and was spread by hand. The inoculant was a water extract of a peat which had become acid because of exposure to windblown sulphur dust. For the acid treatments each plot received 21.2 litres of the various strength acid solutions. This was equivalent to 0.3 cm of rain. The lime used was finely ground $CaCO_3$, (100 mesh) and was spread by hand.

3.3.2 Rate of SO2 Uptake (Laboratory Experiment)

The soil samples with lichen intact were taken from Richardson, 100 km NE of the SO2 emission source. The characteristics of this soil are described in Appendix Table 6. The soil samples were collected in the same way like in section 3.3.1. They were placed in plastic containers with surface area of 95 cm^2. The samples were wrapped in plastic bags and brought into the laboratory for SO2 exposure. At the end of the exposure period, the lichen material was separated from the top 2.5 cm of soil, dried, ground and analyzed for pH, sulphate-sulphur and total sulphur. Results of sulphur gained were expressed in ppm and kg/ha.

3.3.3 Experimental plots

Samples were obtained three times during the course of the experiment:

1. June, 1976 (before the treatments were applied);
2. September, 1976; and
3. June, 1977.

A custom-made soil sampler of 3.5 cm inside diameter was used for soil sampling. The following depths were sampled:

0 - 2.5 cm
2.5 - 15.0 cm
15.0 - 30.0 cm
30.0 - 60.0 cm
60.0 - 90.0 cm
90.0 - 120.0 cm (where possible)

The lichen or moss was sampled by removing a 15 cm square block with a knife. Soils samples were air dried and ground (20 mesh) for analyses.

3.3.4 Precipitation sampling

Rainfall measurements were recorded each month from rain gauges with mineral oil added to prevent evaporation. Incident rain samples were collected by plastic bottles with a 13 cm inside diameter funnel fitted on the top. A wire screen was placed in the funnel to prevent insects from contaminating the rain sample. All the rain samples were obtained from the three experimental plot sites once a month from May to September, 1976. The rain samples brought to the laboratory were filtered through Whatman no. 42 filter paper and analyzed for pH and sulphate-sulphur.

3.3.5 Chemical analyses

pH -- determined using glass electrodes and a Fisher Acumet model 250 digital pH meter. Lichen to water ratio was 1:20. Soil to water ratio was 1:2.5.

Sulphate-sulphur -- determined using Dean's (Dean, 1966) modification of the spectrophotometric method of Johnson and Nishita (1952). The extractant ratio for lichen was 1 g lichen:50 ml 0.1M $CaCl2$.

Total sulphur -- Soil samples were ground and passed through 100-mesh screen.Samples of 0.1 g lichen and 0.2 g soil were used for analyses. Method follows Tabatabai and

Bremner (1976), "an alkaline oxidation method for determination of total sulfur in soils".

Cations -- determined by atomic absorption using a Perkin-Elmer model 503 atomic absorption spectrophotometer with an air-acetylene flame. Ca^{++} and Mg^{++} determinations were first diluted with 1% La2O3 solution to reduce chemcial interference.A nitrous oxide-acetylene flame was used for Al^{+++}.

Elemental sulphur -- modified Hart (1961) method for determining elemental sulphur levels in soils and water.

Electrical conductivity -- 1:2 soil:water ratio; 1:10 lichen:water ratio. Conductivity of the saturation extract measured using a Wheatstone bridge. Values were converted to saturation paste method.

3.4 Movement of Applied Sulphur in Forest Soils

All three experimental sites received the following treatments in June, 1976:

T1 = nil

T2 = 56 kgS/ha as K2SO4

T3 = 112 kgS/ha as K2SO4

The K2SO4 was applied as granules, top dressed by hand. The method and times of sampling were described in section 3.3.3.

Soil samples were air dried and ground (20 mesh) for determinations of pH, sulphate-sulphur and total sulphur, cations and electrical conductivity.

3.5 Soil Acidification and Liming Experiment

Site location and description are given in Figures 1, 4, 5 and 6. The treatments applied to the three sites are given in Table 1. The AOSERP Camp site received all the treatments while the Thickwood Hills site and the Ruth Lake site received treatments 1, 3, 6 and 8 only. All the treaments except 4 and 7 were applied in June, 1976. For treatments 4 and 7, half of the amounts were applied in June, 1976 and the remainder in September, 1976. All treatments were replicated four times. The soils were sampled as in section 3.4 and analyzed for pH, sulphate-sulphur, total sulphur, and elemental sulphur where applicable.

3.6 Sulphur Uptake by Lichen-covered Soil (Field Experiment)

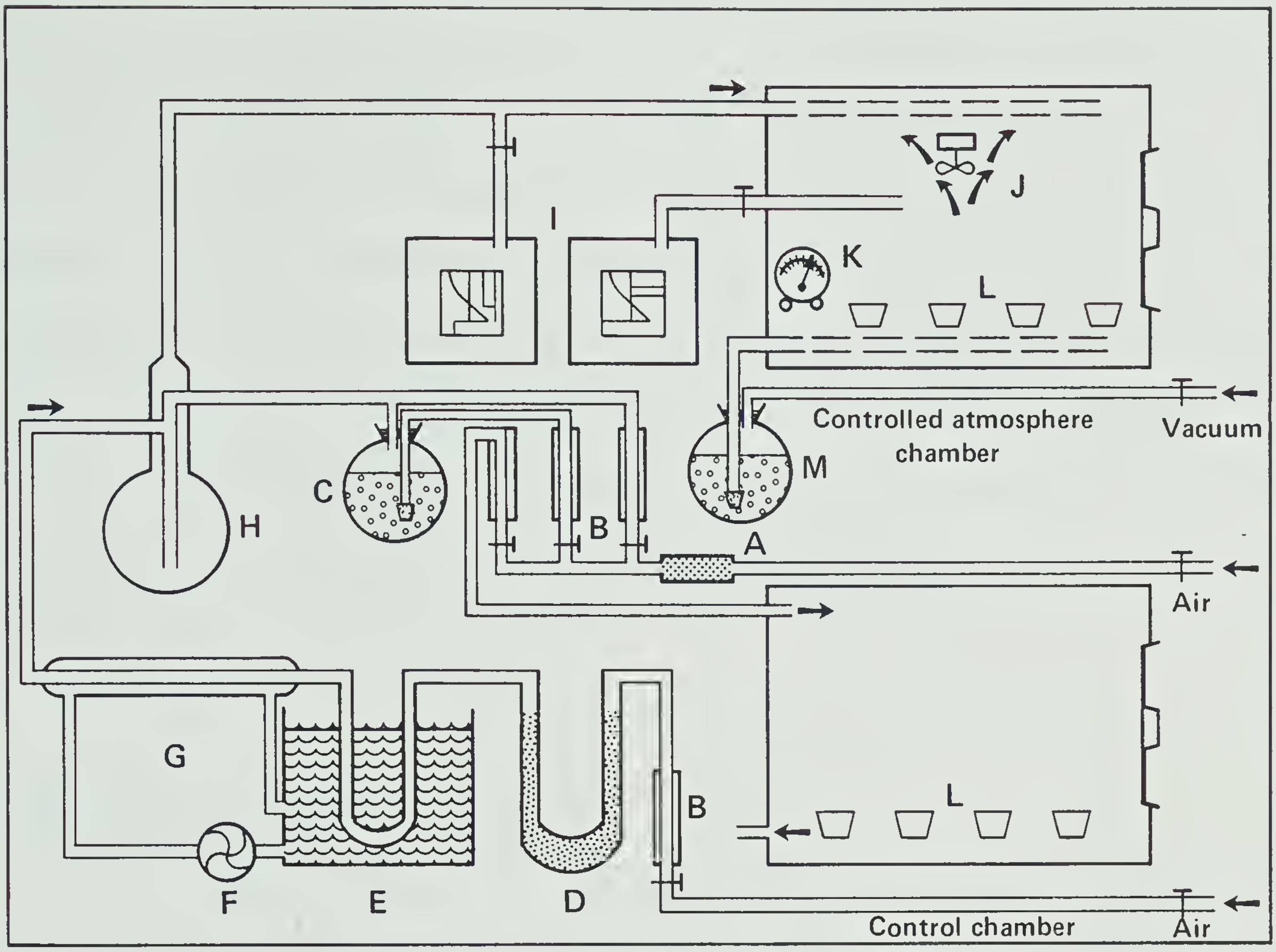
Locations and descriptions of the four SO2 monitoring stations are given in Figure 2 and in section 3.1.4. Soil sampling and analyses produres are given in section 3.3.1. The objective of the experiment was to measure the rate of SO2 uptake by lichen-covered soil from an SO2 emission source. Six replicates of soil samples were set out under rain shelters so that the gain of sulphur by lichen and soil would be directly from the air.

3.7 Sulphur Uptake by Lichen-covered Soil (Controlled Atmosphere Experiment)

Soil sampling and analyses are given in section 3.3.2. Lichen-covered soil samples in plastic containers were exposed to 100 ppb SO2 in a controlled atmosphere apparatus (Figure 7) of 60cm x 60cm x 41.5cm in volume for seven days at two relative humidity levels (20% and 80%). The average air flow rate used was 685 l/hr and the average air temperature was 22°C. In the control chamber, samples were exposed to the same conditions except SO2 was excluded. Six replicates were used for each run.

3.7.1 Operation of the Controlled Atmosphere Apparatus

The apparatus contained the SO2 chamber with humidity level regulated and the control chamber with SO2 excluded. Two inlets of air, one with moisture regulated and one with SO2 concentration regulated were mixed in the mixing bulb (H) before reaching the SO2 chamber. One inlet of air was first passed through silica gel (A) to remove some of its moisture and then was distributed to the control chamber or to the air saturator (C). The flow meters (B) regulated dried air and air moistened to the desired humidity level and was mixed in the mixing bulb (H). Another inlet of air, also regulated by a flow meter (B), was first purified by SO2 absorbing crystals (D) before reaching the constant temperature bath (E). This warmed air was then passed through a condenser (G) containing a SO2 permeation tube



A. Air drying agent (silica gel)
B. Flowmeters
C. Air saturator
D. SO_2 absorbing crystals
E. Constant temperature bath
F. Pump
G. Permeation tube chamber
H. Mixing bulb
I. SO_2 Analyzers (Scientific Industries Inc. Model No. 67)
J. Fan
K. % relative humidity meter
L. Plastic pots with lichens and soils
M. SO_2 trap (30% H_2O_2)

Fig. 7 Controlled Atmosphere Apparatus

releasing SO_2 into the mixing bulb (H). Since permeation rate is a function of temperature, the water in the bath was constantly circulated by a pump (F). The air containing SO_2 and moisture was mixed in the SO_2 chamber by a fan (J) and then removed by vacuum. Before reaching the vacuum, the unused SO_2 was removed by the SO_2 trap (M) containing 30% hydrogen peroxide. Two SO_2 analyzers (I) were used to detect SO_2 concentrations just before reaching the SO_2 chamber and inside the chamber. Any variation in SO_2 concentration was regulated by adjusting water bath temperature (E) and flow of air (B).

3.8 Acidification on mosses

The main objective of the experiment was to determine the extent to which the growth of mosses was affected by acidity. Diluted H_2SO_4 was added to acidify the growing medium to different pH levels for 30 days. In this greenhouse experiment, it was found that all of the mosses tested showed injurious effects when pH of the growing medium was below 3.5. The four species of mosses used in this experiment were:

1. *Hylocomium splendens*
2. *Plaurocium scherberi*
3. *Ptilium crista-castrensis*
4. *Polytricum strictum*

The pH and bulk density of the mosses are given in Appendix Table 27. Mosses collected from the field were cut

into layers 5 cm thick of mostly live mosses and were laid down on the 10 cm thick vermiculite as a growing medium. The 0.1N H_2SO_4 was added to acidify the growing medium with pH adjusted to 2.5, 3.0, 3.5, 4.0 and 4.5. The mosses were laid on top of the vermiculite soaked with acid. During the course of the experiment, pH of the vermiculite was adjusted frequently by adding acid to the side of the pan. The moss surface was never acidified.

3.8.1 Buffering capacity of mosses

Mosses have a marked ability to buffer against the change in pH. In order to determine the amount of acid required to lower the pH of the mosses to a certain level, buffer curves needed to be developed. A 125 cm^3 portion of live moss was shaken in 100 ml of sulphuric acid of different normalities in Erlenmeyers for a week until pH readings stabilized. The equivalent amount of acid required to maintain a certain pH level was plotted to give the buffering capacity curves for the four mosses.

4. RESULTS AND DISCUSSION

4.1 Movement of Applied Sulphur as K_2SO_4 in Forest Soils

The field experiment was designed to determine the movement of sulphur into soil profiles, using top dressed granular K_2SO_4 applied on three forest soils. Since SO_2 absorbed by soil is apparently converted to sulphate, it would be informative to know how the movement of sulphur would affect soil at lower depths. The movement of sulphur could be more accurately measured with the use of radioactive sulphur (S^{35}) in laboratory or field experiments, but especially in long-term field experiments the decay of the S^{35} would be a disadvantage.

The movement of sulphur was measured here by the increase in sulphate-sulphur content at different depths in the soil profiles at the three sites (Appendix Tables 7, 8, and 9). These soils are naturally low in sulphate-sulphur, except for the 0 - 2.5 cm layer of the Thickwood Hills site. Results show that sulphate-sulphur moved readily down the soil profiles after four months of K_2SO_4 application indicated by the increase in sulphate-sulphur down to 60 cm depth. With the heavier rates of K_2SO_4 application, greater amounts of sulphate-sulphur were found. Despite the increase of sulphate-sulphur at various depths, most of them are not statistically significant. Sulphate content of the profiles increased after four months of K_2SO_4 application, but decreased after twelve months indicating that K_2SO_4 had been

completely dissolved and sulphate-sulphur had moved downward to at least 60 cm depth in twelve months time. Most of the downward movement took place within a few summer months with considerable amounts of rainfall. There was generally movement of sulphate-sulphur into the 30 - 60 cm depth after four months. Soil pH did not vary with K2SO4 application (Appendix Table 10).

The movement and fate of sulphur was best indicated by the total sulphur content of soil (Appendix Tables 11, 12, and 13). Sulphate-sulphur not only moved downward, some of it was tied up in the non-extractable forms. The total sulphur content of the different depths increased at all three sites, with the top 2.5 cm of mineral soil increasing the most. Unlike sulphate-sulphur, total sulphur in the soil profiles seemed to have increased with time. Perhaps the longer the sulphate-sulphur remained at a certain depth in the soil profile, the more of it would be expected to be tied up in the organic fraction. Determination of sulphate-sulphur alone is not sufficient to indicate the precise movement of sulphur. There could be a small, or not noticeable, increase of soluble sulphur at a certain depth in the soil profile and yet there could be a substantial increase in total sulphur content.

A small amount of the applied sulphur was not recovered after twelve months (Tables 2, 3, and 4). This could be due to several factors: (1) some of the sulphate-sulphur had moved deeper than 90 cm depth not measured in this case; (2)

Table 2. Soluble sulphate-sulphur and total sulphur content of a sandy soil (AOSERP Camp site) twelve months after K2S04 application.

		S04-S(kg/ha)		Total S(kg/ha)	
Treatments	Depth(cm)	Gross	Net	Gross	Net
Control	2.5- 0.0	4.0		31	
	0.0- 2.5	21.1		55	
	2.5-15.0	4.1		34	
	15.0-30.0	7.4		35	
	30.0-60.0	2.3		39	
	60.0-90.0	4.4		31	
56 kgS/ha	2.5- 0.0	2.0	-2.0	31	0
	0.0- 2.5	26.0	+4.9	62	+ 7
	2.5-15.0	4.2	+0.1	45	+11
	15.0-30.0	7.9	+0.5	49	+12
	30.0-60.0	7.1	+4.8	44	+ 5
	60.0-90.0	8.2	+3.8	32	+ 8
	Total recovery		12.1		43
	Loss		43.9		13
112 kgS/ha	2.5- 0.0	3.9	-0.1	37	+ 6
	0.0- 2.5	24.8	+3.7	99	+44
	2.5-15.0	8.7	+4.6	68	+34
	15.0-30.0	10.5	+3.1	46	+11
	30.0-60.0	7.4	+5.1	41	+ 3
	60.0-90.0	5.7	+1.3	33	+ 2
	Total recovery		17.1		100
	Loss		94.9		12

Table 3. Soluble sulphate-sulphur and total sulphur content of a sandy soil (Ruth Lake site) twelve months after K2SO4 application.

Treatments	Depth(cm)	SO4-S(Kg/ha) Gross	SO4-S(Kg/ha) Net	Total S(Kg/ha) Gross	Total S(Kg/ha) Net
Control	2.5- 0.0	9.2		53	
	0.0- 2.5	5.7		80	
	2.5-15.0	1.9		38	
	15.0-30.0	3.3		37	
	30.0-60.0	2.3		35	
	60.0-90.0	2.7		25	
56 kgS/ha	2.5- 0.0	7.2	-2.0	54	+ 1
	0.0- 2.5	3.4	-2.3	99	+19
	2.5-15.0	1.6	-0.3	53	+15
	15.0-30.0	2.4	-0.9	40	+ 3
	30.0-60.0	2.6	+0.3	39	+ 4
	60.0-90.0	2.7	0.0	27	+ 2
	Total recovery		-5.2		44
	Loss		61.2		12
112 kgS/ha	2.5- 0.0	7.8	-1.4	57	+ 4
	0.0- 2.5	4.6	-1.1	119	+39
	2.5-15.0	1.9	0.0	58	+20
	15.0-30.0	4.2	+0.9	50	+13
	30.0-60.0	2.6	+0.3	41	+ 6
	60.0-90.0	3.4	+0.7	30	+ 5
	Total recovery		-0.6		87
	Loss		112.6		25

Table 4. Soluble sulphate-sulphur and total sulphur content of a clay loam soil (Thickwood Hills site) twelve months after K2SO4 application.

		SO4-S(Kg/ha)		Total S(Kg/ha)	
Treatments	Depth(cm)	Gross	Net	Gross	Net
Control	2.5- 0.0	2.0		60	
	0.0- 2.5	45.3		63	
	2.5-15.0	9.9		54	
	15.0-30.0	9.5		46	
	30.0-60.0	7.2		47	
	60.0-90.0	6.7		39	
56 kgS/ha	2.5- 0.0	3.7	+1.7	60	0
	0.0- 2.5	47.6	+2.3	80	+17
	2.5-15.0	9.6	-0.3	65	+11
	15.0-30.0	9.6	+0.1	54	+ 8
	30.0-60.0	6.8	-0.4	53	+ 6
	60.0-90.0	8.4	+1.7	45	+ 6
	Total recovery		5.1		48
	Loss		50.9		8
112 kgS/ha	2.5- 0.0	5.7	+3.7	65	+ 5
	0.0- 2.5	46.8	+1.5	107	+44
	2.5-15.0	19.1	+9.2	80	+26
	15.0-30.0	15.5	+6.0	56	+10
	30.0-60.0	11.6	+4.4	56	+ 9
	60.0-90.0	3.2	-3.5	44	+ 5
	Total recovery		21.3		99
	Loss		90.7		13

sulphate-sulphur might have moved laterally beyond the plot boundary; (3) some of the sulphate-sulphur might have been taken up by plants; and (4) sulphate-sulphur might have been lost into the air, perhaps like denitrification of soil nitrogen.

Electrical conductivity was measured at the end of the experiment to detect salt content of different layers (Tables 5, 6, and 7). Results indicate that after twelve months, salt content of sandy soil profiles had returned to levels similar to those of the control treatment, except the lichen and moss layer and the top 2.5 cm of mineral soil at the AOSERP camp site. The Thickwood Hills site with heavier soil texture showed a small accumulation of salt at the deeper layers.

The movement of K2SO4 was also evidenced by the increase in potassium at different layers (Tables 8, 9, and 10). Of the three profiles, the soil with a heavier texture gained the most potassium, as expected. Most of the adsorbed potassium was found in the 25 to 30 cm depth. As K2SO4 moved downward, cation exchange took place. Other cations were replaced by the mass action of potassium. Of the four cations analyzed (Tables 5, 6, and 7) calcium was exchanged most, followed by magnesium. Potassium had little effect on exchange for manganese and aluminum.

This experiment showed that sulphate-sulphur moved readily down the soil profiles during the relatively wet summer season. As sulphate-sulphur moved, some of it was

Table 5. Electrical conductivity and the amount of extractable cations (ppm) of K2SO4 experiment at the AOSERP Camp site (June, 1977).

			Extractable cations (ppm)				
Treatments	Depth(cm)	E.C. mmhos/cm	K^+	Ca^{++}	Mg^{++}	Mn^{++}	Al^{+++}
Control	2.5- 0.0	0.28a	45.7a	213.1	21.0	11.2	3.0
	0.0- 2.5	0.11a	28.7a	153.2	52.6	51.1	3.9
	2.5-15.0	0.09a	12.7a	146.1	49.8	39.8	3.9
	15.0-30.0	0.06a	16.4a	100.2	48.8	19.0	3.4
	30.0-60.0	0.05a	9.4a	110.2	48.4	16.5	3.3
	60.0-90.0	0.03a	10.0a	147.3	49.7	17.1	3.5
K2SO4 @ 56 KgS/ha	2.5- 0.0	0.35ab	54.0b	209.0	20.0	9.6	2.9
	0.0- 2.5	0.17a	36.5b	135.7	46.3	48.2	3.8
	2.5-15.0	0.09a	17.5b	136.0	37.4	37.1	3.9
	15.0-30.0	0.07a	18.4ab	97.2	44.8	11.9	3.1
	30.0-60.0	0.09a	10.0a	108.2	48.0	11.7	3.2
	60.0-90.0	0.06a	11.3a	141.1	48.0	16.1	3.5
K2SO4 @ 112 KgS/ha	2.5- 0.0	0.40b	62.0b	208.0	19.8	7.1	2.9
	0.0- 2.5	0.39b	52.1b	104.5	42.4	47.2	3.8
	2.5-15.0	0.10a	23.4b	130.1	40.0	34.6	3.7
	15.0-30.0	0.11a	21.0b	86.6	41.8	10.0	2.9
	30.0-60.0	0.10a	11.3a	82.4	45.2	10.1	3.2
	60.0-90.0	0.09a	11.4a	117.6	46.2	16.0	3.3

For any soil depth in each column, values are statistically different when followed by different letters.

Table 6. Electrical conductivity and the amount of extractable cations (ppm) of K2S04 experiment at the Ruth Lake site (June, 1977).

			Extractable cations (ppm)				
Treatments	Depth(cm)	E.C. mmhos/cm	K^+	Ca^{++}	Mg^{++}	Mn^{++}	Al^{+++}
Control	2.5- 0.0	0.69a	78.0a	250.0	24.0	8.9	3.2
	0.0- 2.5	0.28a	28.2a	120.0	38.0	19.5	4.2
	2.5-15.0	0.17a	14.6a	75.0	39.0	18.0	4.6
	15.0-30.0	0.16a	14.8a	70.5	38.2	15.0	4.5
	30.0-60.0	0.15a	14.8a	70.0	36.0	14.8	3.3
	60.0-90.0	0.13a	15.7a	73.5	37.0	15.0	3.2
K2S04 @ 56 KgS/ha	2.5- 0.0	0.66a	82.1a	232.0	21.3	7.3	3.0
	0.0- 2.5	0.30a	34.2a	110.0	36.5	18.0	4.0
	2.5-15.0	0.18a	15.9a	70.0	36.3	18.0	4.0
	15.0-30.0	0.18a	15.0a	70.0	33.3	13.0	4.2
	30.0-60.0	0.15a	17.8a	67.0	35.5	13.5	3.2
	60.0-90.0	0.13a	17.0a	65.0	37.0	13.8	3.0
K2S04 @ 112 KgS/ha	2.5- 0.0	0.73a	103.5b	204.0	18.2	7.0	2.7
	0.0- 2.5	0.32a	35.5a	100.5	33.8	18.0	4.0
	2.5-15.0	0.16a	23.2b	66.0	35.3	10.7	3.5
	15.0-30.0	0.15a	24.2b	65.0	35.0	12.0	3.3
	30.0-60.0	0.17a	15.9a	60.2	35.2	12.9	2.8
	60.0-90.0	0.13a	16.2a	60.0	36.0	10.8	3.0

For any soil depth in each column, values are statistically different when followed by different letters.

Table 7. Electrical conductivity and the amount of extractable cations (ppm) of K2SO4 experiment at the Thickwood Hills site (June, 1977).

			Extractable cations (ppm)				
Treatments	Depth(cm)	E.C. mmhos/ cm	K^+	Ca^{++}	Mg^{++}	Mn^{++}	Al^{+++}
Control	2.5- 0.0	0.56a	93.2a	230.0	27.3	10.5	3.5
	0.0- 2.5	0.29a	287.5a	1086.0	240.8	18.5	12.0
	2.5-15.0	0.22a	133.3a	723.0	120.0	16.2	10.5
	15.0-30.0	0.13a	195.5a	1275.5	220.6	16.0	10.0
	30.0-60.0	0.13a	111.0a	1376.0	286.3	15.7	10.0
	60.0-90.0	0.12a	107.5a	1345.0	275.0	15.0	8.0
K2SO4 @ 56 kgS/ha	2.5- 0.0	0.55a	96.0a	224.0	23.0	9.8	3.3
	0.0- 2.5	0.25a	293.2a	1068.0	238.8	14.8	11.5
	2.5-15.0	0.26a	141.5a	711.0	108.5	16.0	10.4
	15.0-30.0	0.21b	199.8a	1270.0	220.0	16.0	10.2
	30.0-60.0	0.24b	117.5a	1359.0	282.2	15.2	10.2
	60.0-90.0	0.23a	110.0a	1340.0	274.5	14.8	7.5
K2SO4 @ 112 kgS/ha	2.5- 0.0	0.55a	103.7a	212.0	21.5	9.4	3.3
	0.0- 2.5	0.36b	302.0a	1030.0	230.0	14.4	11.2
	2.5-15.0	0.27a	148.5a	702.5	98.0	15.7	10.2
	15.0-30.0	0.23b	205.4a	1262.0	215.0	15.5	10.2
	30.0-60.0	0.21b	123.3a	1335.5	270.5	15.0	10.0
	60.0-90.0	0.15a	113.7a	1332.0	270.0	15.0	7.8

For any soil depth in each column, values are statistically different when followed by different letters.

Table 8. Amount of extractable K (kg/ha) at the AOSERP Camp site of K2SO4 experiment (June, 1977).

Treatments	Depth(cm)	Extractable K (kg/ha)		Increase
Control	2.5- 0.0	2.8		
	0.0- 2.5	56.0		
	2.5-15.0	33.3		
	15.0-30.0	49.0		
	30.0-60.0	30.4		
	60.0-90.0	35.5		
K2SO4 @ 56 kgS/ha	2.5- 0.0	3.3		+ 0.5
	0.0- 2.5	71.2		+ 15.2
	2.5-15.0	45.8		+ 12.5
	15.0-30.0	54.9		+ 5.9
	30.0-60.0	32.3		+ 1.9
	60.0-90.0	40.1		+ 4.6
			Total	+ 40.6
K2SO4 @ 112 kgS/ha	2.5- 0.0	3.8		+ 1.0
	0.0- 2.5	101.6		+ 45.6
	2.5-15.0	61.5		+ 28.2
	15.0-30.0	62.7		+ 13.7
	30.0-60.0	36.5		+ 6.1
	60.0-90.0	40.4		+ 4.9
			Total	+ 99.5

Table 9. Amount of extractable K (Kg/ha) at the Ruth Lake site of K2SO4 experiment (June, 1977).

Treatments	Depth(cm)	Extractable K (Kg/ha)		Increase
Control	2.5- 0.0	7.1		
	0.0- 2.5	64.5		
	2.5-15.0	39.1		
	15.0-30.0	44.4		
	30.0-60.0	47.8		
	60.0-90.0	53.3		
K2SO4 @ 56 KgS/ha	2.5- 0.0	7.5		+ 0.4
	0.0- 2.5	78.2		+ 13.7
	2.5-15.0	42.6		+ 3.5
	15.0-30.0	45.0		+ 0.6
	30.0-60.0	57.5		+ 9.7
	60.0-90.0	57.8		+ 4.5
			Total	+ 32.4
K2SO4 @ 112 KgS/ha	2.5- 0.0	9.4		+ 2.3
	0.0- 2.5	81.1		+ 16.6
	2.5-15.0	62.3		+ 23.2
	15.0-30.0	72.7		+ 28.3
	30.0-60.0	51.4		+ 3.6
	60.0-90.0	55.2		+ 1.9
			Total	+ 75.9

Table 10. Amount of extractable K (kg/ha) at the Thickwood Hills site of K2SO4 experiment (June, 1977).

Treatments	Depth(cm)	Extractable K (kg/ha)		Increase
Control	2.5- 0.0	7.1		
	0.0- 2.5	438.1		
	2.5-15.0	249.8		
	15.0-30.0	428.1		
	30.0-60.0	262.0		
	60.0-90.0	262.1		
K2SO4 @ 56 KgS/ha	2.5- 0.0	7.3		+ 0.2
	0.0- 2.5	446.8		+ 8.7
	2.5-15.0	265.2		+ 15.4
	15.0-30.0	437.6		+ 9.5
	30.0-60.0	277.9		+ 15.9
	60.0-90.0	268.1		+ 6.0
			Total	+ 55.7
K2SO4 @ 112 KgS/ha	2.5- 0.0	7.9		+ 0.8
	0.0- 2.5	460.2		+ 22.1
	2.5-15.0	278.2		+ 28.5
	15.0-30.0	449.9		+ 21.8
	30.0-60.0	291.1		+ 29.1
	60.0-90.0	277.2		+ 15.1
			Total	+117.4

converted to the non-extractable form, the mechanism for which is unknown. Sulphate-sulphur can move as deep as 60 cm, or deeper, in less than twelve months. As sulphate-sulphur moved downward, its accompanying K replaced cations like Ca and the leaching of cations would affect the chemistry of soil. One could speculate that sulphate-sulphur added as SO2 emissions to the three soils would result in leaching of Ca and Mg.

4.2 Soil Acidification and Liming Experiment

Elemental sulphur and diluted sulphuric acid were top dressed on forest soils in June, 1976 at the three locations to determine the rate and effects of acidification on forest soils. The movement of sulphur was also determined in the three soil profiles. Lime was used to counteract soil acidity caused by elemental sulphur oxidation. Soil samples from the treatments were taken four and twelve months after applications and pH, sulphate-sulphur and elemental sulphur contents were determined.

4.2.1 Soils Acidified by Elemental Sulphur

Elemental sulphur is a by-product of gas processing. The process removes sulphur from sour gas which contains large amounts of hydrogen sulfide. The elemental sulphur is removed from the gas and solidified into stockpiles. The handling of the elemental sulphur and the blowing of fine sulphur dust may cause soil acidity problems within a few km

of stockpiles. The oil extracting plants also produce elemental sulphur and store it in stockpiles. This experiment simulates the problem of elemental sulphur acidification near gas processing or oil extracting plants. Fine elemental sulphur was top dressed onto soils at three rates at the AOSERP Camp site and at one rate at the Ruth Lake and Thickwood Hills sites to determine the rate and effects of acidification on vegetation and soils.

4.2.1.1 Effects on soil pH and vegetation

Soils at the three sites were naturally acidic with soil pH ranging from 4.0 to slightly under 6.0 (Appendix tables 14, 15, and 16). After four months of treatment, oxidation of elemental sulphur caused soil acidification mainly in the top 2.5 cm of the profiles lowering soil pH by about 0.3 unit in a sandy soil and 0.2 unit in a clay loam soil. Soil pH values at lower depths were also lowered, however, they were not significantly different from the control (Appendix Tables 14, 15, and 16). After twelve months of elemental sulphur application, soil acidification extended to the 15 cm depth in sandy soils, but the clay loam soil at the Thickwood Hills site showed a smaller decrease in soil pH. Soil pH at lower depths tended to decrease more as time went on, indicating when more elemental sulphur was oxidized, acidity moved further down.

Soil pH was depressed the most after four months of elemental sulphur application, and the rate of depression

was less from four to twelve months. Buffering capacity of soils given in Appendix Figures 1 to 5 show that soils respond sharply to initial addition of acid but respond to a lesser extent when more acid is added.

Even though the pH of the vegetative layer was lowered by more than half a unit in some areas, the lichens, (Cladina mitis and C. arbuscula) mosses (principally Polytrichum strictum) and other vegetation such as bearberry (Arctostaphylos uva-ursi) and bog craneberry (Vaccinium vitis-idaea) did not seem to be affected by the change in pH.

4.2.1.2 Effects on sulphur content of soils

Sulphate-sulphur was released as a result of elemental sulphur oxidation as indicated by the increase in sulphate-sulphur content (Appendix Table 17). Most of the soluble sulphur increase was found in the top layer (2.5 cm) of the mineral soil. More sulphate-sulphur was found with a higher rate of application of elemental sulphur. However, the rate of oxidation was not proportional to the rate of elemental sulphur applied.

Elemental sulphur content at different layers was determined (Appendix Table 18) and found to remain mostly in the top layer of mineral soil twelve months after application. Only about 5% of the elemental sulphur applied at 560 Kg/ha was found in the 2.5 - 15.0 cm depth. No elemental sulphur was found lower than 15 cm indicating the

Table 11. Amount of sulphate-sulphur, elemental sulphur (kg/ha) and change in soil pH in a sandy soil (AOSERP Camp site) at four and twelve months after application of elemental sulphur at various rates.

		Sept. 1976		
Treatments	Depth(cm)	SO4-S (kgS/ha)	Elemental S (kgS/ha)	pH
56 kgS/ha	2.5- 0.0	3.6	4.7	-0.16
	0.0- 2.5	32.0	19.5	-0.15
	2.5-15.0	8.1	0.0	-0.13
	15.0-30.0	6.1		-0.01
	30.0-60.0	4.3		+0.01
	60.0-90.0	*		*
280 kgS/ha	2.5- 0.0	12.9	29.6	-0.45
	0.0- 2.5	63.2	120.9	-0.19
	2.5-15.0	8.4	0.0	-0.10
	15.0-30.0	7.8		-0.20
	30.0-60.0	7.4		-0.01
	60.0-90.0	*		*
560 kgS/ha	2.5- 0.0	*	*	*
	0.0- 2.5	*	*	*
	2.5-15.0	*	*	*
	15.0-30.0	*	*	*
	30.0-60.0	*	*	*
	60.0-90.0	*	*	*
280 kgS/ha + lime @ 2500 kg/ha	2.5- 0.0	11.1	21.4	+1.03
	0.0- 2.5	53.4	99.4	+0.17
	2.5-15.0	22.8	0.0	-0.11
	15.0-30.0	17.6		0.00
	30.0-60.0	12.3		-0.07
	60.0-90.0	10.7		0.00

* no soil samples taken

Table 11. Continued.

		June, 1977		
Treatments	Depth(cm)	SO4-S (KgS/ha)	Elemental S (KgS/ha)	pH
56 KgS/ha	2.5- 0.0	1.4	2.8	-0.12
	0.0- 2.5	27.3	13.6	-0.16
	2.5-15.0	2.4	0.0	-0.20
	15.0-30.0	2.1		-0.07
	30.0-60.0	2.6		+0.04
	60.0-90.0	2.8		+0.04
280 KgS/ha	2.5- 0.0	6.6	12.2	-0.42
	0.0- 2.5	80.3	78.0	-0.37
	2.5-15.0	6.8	0.0	-0.46
	15.0-30.0	3.9		-0.32
	30.0-60.0	3.2		-0.19
	60.0-90.0	4.6		-0.13
560 KgS/ha	2.5- 0.0	8.8	38.1	-0.59
	0.0- 2.5	121.5	204.8	-0.54
	2.5-15.0	29.4	70.8	-0.22
	15.0-30.0	8.7	0.0	-0.24
	30.0-60.0	4.8		-0.31
	60.0-90.0	3.9		-0.26
280 KgS/ha + lime @ 2500 Kg/ha	2.5- 0.0	7.1	10.4	+0.02
	0.0- 2.5	51.9	66.3	+0.01
	2.5-15.0	13.6	0.0	-0.16
	15.0-30.0	6.0		-0.03
	30.0-60.0	5.5		-0.12
	60.0-90.0	4.3		-0.05

* no samples taken

Table 12. Amount of sulphate-sulphur, elemental sulphur (Kg/ha) and change in soil pH in a sandy soil (Ruth Lake site) at four and twelve months after application of elemental sulphur at 280 Kg/ha.

	Sept., 1976		
Depth(cm)	SO4-S (kgS/ha)	Elemental S (kgS/ha)	pH
2.5- 0.0	25.7	96.0	-0.79
0.0- 2.5	50.3	80.0	-0.62
2.5-15.0	4.3	0.0	-0.15
15.0-30.0	4.5	0.0	+0.05
30.0-60.0	3.2	0.0	+0.05
60.0-90.0	*	*	*

	June, 1977		
Depth(cm)	SO4-S (kgS/ha)	Elemental S (kgS/ha)	pH
2.5- 0.0	27.6	90.0	-0.38
0.0- 2.5	30.6	66.3	-0.48
2.5-15.0	19.0	0.0	-0.56
15.0-30.0	9.3	0.0	+0.24
30.0-60.0	1.6	0.0	+0.07
60.0-90.0	1.7		-0.01

* no soil samples taken

Table 13. Amount of sulphate-sulphur, elemental sulphur (kg/ha) and change in soil pH in a clay loam soil (Thickwood Hills site) at four and twelve months after application of elemental sulphur at 280 kg/ha.

	Sept., 1976		
Depth(cm)	SO4-S (kgS/ha)	Elemental S (kgS/ha)	pH
2.5- 0.0	16.0	76.8	-0.51
0.0- 2.5	88.2	96.0	-0.26
2.5-15.0	11.1	0.0	-0.13
15.0-30.0	7.9	0.0	-0.05
30.0-60.0	4.0	0.0	-0.04
60.0-90.0	*		*

	June, 1977		
Depth(cm)	SO4-S (kgS/ha)	Elemental S (kgS/ha)	pH
2.5- 0.0	8.2	30.2	-0.45
0.0- 2.5	22.7	83.0	-0.23
2.5-15.0	12.2	0.0	-0.20
15.0-30.0	4.8	0.0	+0.20
30.0-60.0	2.6	0.0	+0.20
60.0-90.0	4.1		+0.20

* no soil samples taken

slow downward movement of elemental sulphur even in a porous soil.

At the Ruth Lake site, much of the elemental sulphur was held by the dense layer of moss causing less elemental sulphur oxidation.

4.2.1.3 Elemental sulphur recovery

The rate of elemental sulphur oxidation at the three sites was estimated by recovering the unoxidized elemental sulphur. In this experiment, the elemental sulphur was added with an "inoculant" consisting of small amounts of a soil which had previously been treated with fine elemental sulphur. Consequently, the oxidation of added elemental sulphur in this experiment was probably speeded through the addition of elemental sulphur oxidizing bacteria. At the end of the experiment, only about 30% (50% after four months) of the elemental sulphur applied was recovered at the AOSERP Camp site at both the 56 and 280 kgS/ha application levels (Table 14). More elemental sulphur (56%) was recovered at the Ruth Lake site due to the thick moss layer (Table 15) and recovery was 40% at Thickwood Hills site (Table 16). The rate of elemental sulphur oxidation was expected to be slow in the first year but would be expected to increase as time went on. This would depend on any factors affecting the growth of sulphur oxidizing bacteria. The three soils studied were capable of oxidizing over a hundred kg of elemental sulphur per ha per year, generating enough acid to

Table 14. Amount of sulphur recovery (kg/ha) at four and twelve months after application of elemental sulphur at various rates on a sandy soil (AOSERP Camp site).

Treatments		Sept.,76	June,77
56 kgS/ha	S° (kgS/ha)	24	16
	Net SO4-S (kgS/ha)	28	34
	Total recovery(kgS/ha)	52	50
	% S° recovery	43	25
280 kgS/ha	S° (kgS/ha)	150	90
	Net SO4-S (kgS/ha)	74	91
	Total recovery(kgS/hA)	224	181
	% S° recovery	54	32
560 kgS/ha	S° (kgS/ha)	*	314
	Net SO4-S (kgS/ha)	*	163
	Total recovery(kgS/ha)	*	491
	% S° recovery		56
280 kgS/ha + Lime @ 2500 kg/ha	S° (kgS/ha)	121	77
	Net SO4-S (kgS/ha)	91	74
	Total recovery(kgS/ha)	212	151
	% S° recovery	43	28

* no soil samples taken

Table 15. Amount of sulphur recovery (kg/ha) at four and twelve months after application of elemental sulphur at 280 kg/ha on a sandy soil (Ruth Lake site).

	Sept.,76	June,77
S° (kgS/ha)	176	156
Net SO4-S (kgS/ha)	59	57
Total recovery(kgS/ha)	235	213
% S° recovery	62.8	55.7

Table 16. Amount of sulphur recovery (kg/ha) at four and twelve months after application of elemental sulphur at 280 kg/ha on a clay loam soil (Thickwood Hills site).

	Sept.,76	June,77
S° (kgS/ha)	173	113
Net SO4-S (KGS/HA)	61	25
Total recovery(kgS/ha)	234	138
% S° recovery	61.8	40.3

lower soil pH. Soils with low base saturation would be susceptible to the acidity which in turn causes damages to more sensitive vegetation.

4.2.2 Soils Acidified by Sulphuric Acid

The experiment simulated interception of acid rain by forest soils which affects both soils and vegetation. Acid rain would not be as strong as the diluted sulphuric acid used in the experiment and the accumulation of sulphur in a natural environment would be gradual, but in order to forsee the effects of acidification on forest soils in a one year experiment, a stronger acid needed to be used to speed up the effects. In this case, 0.1N and 0.5N sulphuric acid were sprinkled resembling 0.3 cm of rain.

4.2.2.1 Effects on soil pH and vegetation

The effects of soil acidification by diluted sulphuric acid were much more pronounced than those induced by elemental sulphur. Soil pH was significantly depressed to levels of 15 cm at an application rate of 280 kgS/ha treatment in a sandy soil four months after application (Appendix Table 19). However, all soil depths showed pH depression down to 90 cm. Smaller amounts of acid (56 kgS/ha) showed less effects. At the end of twelve months, acid had probably moved deeper than 120 cm but these levels were not sampled (Appendix Tables 20, 21, and 22). The rapid downward movement of diluted acid in the soil profiles was

clearly indicated by the drop in soil pH throughout all the depths sampled. The acid moved readily in both sandy and clay loam soils.

Diluted sulphuric acid had damaging effects on vegetation. At all three sites, lichen which received diluted acid, regardless of amount, showed damaging effects. They turned yellowish and stopped new growth a few months after treatment. All mosses also turned brownish and appeared to be weakening. Other higher plants such as grasses, shrubs and trees did not show any damaging effects. They still produced flowers and fruits in the fall. At the end of the experiment, all lichens remained stunted by the acid. The brownish, weak-looking Polytrichum strictum and other species of mosses started to show new growth gradually. All other higher plants appeared normal. The pH of the surface soil at the end of the experiment was above 4.0.

4.2.2.2 Effects on soil sulphur and fate of the applied acid

The movement of acid down the soil profile was closely related to the movement of sulphate-sulphur in this experiment. Where soil pH had been lowered, there was an increase in sulphate-sulphur. Substantial amounts of sulphate-sulphur were moved into the lower depths (Appendix Tables 20, 21 and 22). With 560 kg of sulphur applied as sulphuric acid, the concentration of sulphate-sulphur increased several times higher than with 56 KgS applied in a

sandy soil at the AOSERP Camp site (Appendix table 23). The Ruth Lake site which was also sandy did not show similar results. The concentration of sulphate-sulphur was much lower probably due to the shallow and fluctuating water table. In a wet season, the water table was only about one meter deep. Most of the acid which reached the ground water could be diluted and carried away. This might contribute to the low per cent sulphur recovery at this site.

There was much more sulphur recovery at four months sampling than at twelve months sampling. About half of the sulphur applied was not recovered at the end of the experiment. The unrecovered sulphur could have been lost in several ways similar to the conditions explained in section 4.1. The acid would probably have penetrated deeper than the sampling depth or laterally away from the plot. Also, sulphate-sulphur might have been tied up in other forms not extractable by 0.1 M $CaCl_2$. At the Ruth Lake site where waterlogged (anaerobic) conditions occurred occasionally at lower depths, sulphate-sulphur might have been reduced to sulphides. The amount of sulphur taken up by plants would be minimal comparatively, in the order of less than 10 kg/ha/yr.

4.2.3 Liming Forest Soils

In Alberta, about 17 percent of the cultivated soils are acid (soil pH is 6.0 or less) and about 42 percent of the cultivated soils are susceptible to acidification by

nitrogen and sulphur fertilizers or by SO2 emissions (Nyborg and Walker, 1977). Liming of agricultural soils is a simple technique, but liming of forest soils is usually considered a costly, impractical and seldom-used practice. But perhaps, liming may be the only solution to the acidity problem. Soils which had been severely acidified (pH about 2.0) by windblown elemental sulphur near gas processing plant was found to restore plant growth after liming (Bertrand, 1973).

Different methods have been developed in applying lime in forests where accessibility is limited. Methods such as aerial application, blowing and spraying lime using a hydroseeder and application by hand are used. Each method has its advantages and disadvantages. There is no one method which can be used to meet the various conditions with economy, accuracy and practicality.

In this experiment, 2500 kg of ground limestone (80% passed through 100 mesh sieve) per hectare was top dressed by hand onto the soil surface at the three experimental sites to observe the downward movement of lime and its effects on soils and vegetation. Soil pH was measured four and twelve months after application. Lime was found to move readily in two sandy soils to the 15.0 cm depth, but remained mostly in the surface 2.5 cm in a clay loam soil twelve months after application. The application of 2500 kg/ha of limestone was enough to raise the soil pH by about 1.0 unit but the effect was not lasting. The reaction of lime with soil is slow, therefore the soil pH might still be

changing when measured. More lime (perhaps double the amount) seemed to be required to raise soil pH to near neutrality.

4.2.3.1 Effects on soil, pH, and plants

The pH of surface soil increased substantially in both sandy and clay loam soils after application of lime. There was an increase of more than 1.0 pH unit after four months of application and close to 1.0 pH unit after twelve months in a sandy soil at the AOSERP Camp site (Table 17). The soil at the Ruth Lake site was more acidic naturally and still was 0.4 unit higher than the control after treatment (Table 18). The clay loam soil at the Thickwood Hills site was also benefited by liming. Soil pH was raised more than 0.5 unit in the surface layer even twelve months after application (Table 19). A small amount of lime might have diffused deeper than 2.5 cm depth causing a slight increase in soil pH, however, soils below 15.0 cm were not affected.

Top dressing of lime on forest soils had no effect on vegetation, therefore, it could be useful in preventing soil acidity where soils are susceptible to acidification by long term sulphur deposition from SO2 emissions.

4.2.3.2 Liming plots receiving elemental sulphur

Plots which received 280 kg elemental sulphur per ha, 2500 kg of limestone per ha were also top dressed to observe the effects of liming. The results indicate that soils which

Table 17. Soil pH values of a sandy soil (AOSERP Camp site) at four and twelve months after the application of lime at 2500 kg/ha.

	Soil pH in Sept., 1976			Soil pH in June, 1977		
Depth(cm)	Control	Limed	Difference	Control	Limed	Difference
2.5- 0.0	4.48	6.29	+1.81	4.42	5.43	+1.03
0.0- 2.5	5.09	6.48	+1.39	5.14	6.33	+1.19
2.5-15.0	5.64	5.95	+0.31	5.66	5.84	+0.18
15.0-30.0	5.66	5.66	0.00	5.66	5.68	+0.02
30.0-60.0	5.84	5.81	-0.03	5.81	5.78	-0.03
60.0-90.0	5.94	5.93	-0.01	5.86	5.86	0.00

Table 18. Soil pH values of a sandy soil (Ruth Lake site) at four and twelve months after the application of lime at 2500 kg/ha.

	Soil pH in Sept., 1976			Soil pH in June, 1977		
Depth(cm)	Control	Limed	Difference	Control	Limed	Difference
2.5- 0.0	4.34	6.34	+2.00	4.44	6.26	+1.82
0.0- 2.5	4.56	5.40	+0.84	4.61	4.99	+0.38
2.5-15.0	4.95	5.13	+0.18	5.02	5.12	+0.10
15.0-30.0	5.25	5.23	-0.02	5.07	5.09	+0.02
30.0-60.0	5.57	5.50	-0.07	5.37	5.37	0.00
60.0-90.0	5.57	5.56	-0.01	5.43	5.41	-0.02

Table 19. Soil pH values of a clay loam soil (Thickwood Hills site) at four and twelve months after the application of lime at 2500 kg/ha.

	Soil pH in Sept., 1976			Soil pH in June, 1977		
Depth(cm)	Control	Limed	Difference	Control	Limed	Difference
2.5- 0.0	4.75	6.35	+1.60	4.80	6.10	+1.30
0.0- 2.5	5.07	6.85	+0.78	5.20	5.88	+0.68
2.5-15.0	5.18	5.24	+0.06	5.20	5.22	+0.02
15.0-30.0	5.39	5.38	-0.01	5.15	5.14	-0.01
30.0-60.0	5.65	5.59	-0.06	5.47	5.26	-0.21
60.0-90.0	5.96	5.94	-0.02	5.65	5.54	-0.11

had been acidified 0.19 pH unit were raised 0.17 unit with liming four months after application (Appendix Table 14). More elemental sulphur was oxidized when lime was added. As a result, less elemental sulphur was recovered. The slow downward movement of lime, however, was not able to neutralize soil acidity below 15 cm. The subsoil still remained acidified at the end of the experiment. Only through mixing lime could the subsoil be neutralized in shorter time. Lime will diffuse downward slowly but it will take years.

4.2.3.3 Downward movement of lime in forest soils

In general, lime is considered to be slow in penetrating subsoil when not incorporated. But Longnecker and Sprague (1940) believed that lime does diffuse downward slowly over time. The results of the present experiment indicate that top dressed lime on a permeable sandy soil diffused downward slowly in twelve months causing soil pH at 15 cm depth to rise about 0.1 to 0.2 unit (Table 17). The clay loam soil, however, restricted lime movement downward and most of the lime remained in the surface 2.5 cm depth as shown by the pH values (Table 19). A small amount of lime might have moved deeper down in the soils causing a slight increase in soil pH, but, this was not true statistically. At the Ruth Lake site where the moss layer was thick and dense, downward movement of lime was also restricted (Table 18). Soil pH ,therefore, did not rise as much as in the

AOSERP Camp area where soil was also sandy.

4.3 Dry Deposition

Approximately half a million tons of sulphur dioxide gas are emitted annually in Alberta, by gas processing plants and during extraction of oil from oil sands (Hocking and Nyborg, 1974). Some of the SO2 gas was brought down in precipitation but it is far less (about one tenth) than the amount deposited directly on soil or absorbed by surface water, or vegetation (Nyborg *et al*., 1973). It seems that when soils are not frozen, more SO2 is absorbed directly by soils than by vegetation or water, at least in agricultural areas. Thus, dry deposition is an important mechanism by which the emitted sulphur is returned to the surface of the earth. Both field and laboratory experiments were carried out in this study to determine the rates of sulphur deposition and rates of acidification of soils and lichens, by exposing samples of lichen-covered soil near an SO2 emission source in the field and in a controlled atmosphere. Both experiments showed that lichens and soils were capable of absorbing substantial amounts of SO2.

4.3.1 Sulphur Uptake by Lichen-covered Soil (Field Experiment)

Intact lichen-covered soil samples in plastic containers were set out under rain shelters at four locations from May to October, 1977 (Fig. 2). The samples

were placed under rain shelters so that any sulphur addition to lichen or soil would only originate from the air. The results of the effects of SO2 emissions on soil pH, soluble sulphur and total sulphur content are given in Table 20. The Steepbank #2 and Muskeg Mountain sites were closest to the SO2 emission source, and were considered to be exposed sites. Algar and May sites were at least 100 km away from the SO2 emission source, and were considered to be control sites.

The differences in pH change and soluble sulphur change were not great, but the increase in total sulphur content in the exposed soil was substantial. A six-month experimental period may be too short to establish any definite results, but total sulphur determination is an important analyses that should be looked into.

4.3.1.1 The effects of SO2 emissions on soil pH

Determination of soil pH is a common method to identify the acidity or alkalinity of soils, but because of seasonal fluctuations by biological activities, slight changes in soil pH might occur even though the soils are not affected by SO2 emissions. Bowser and Leat (1958) showed that pH fluctuations of ± 1.0 unit could normally occur within a season. However, Penney and Henry (1976) showed little change from year to year. In order to minimize such errors, six replications were used in this experiment.

After exposure to SO2 emissions for six months, the

Table 20. The rate of sulphur dioxide uptake by intact lichen-covered soil samples set out under cover at four field stations from May to October, 1977. Values are means of six replications.

Site	Layer	pH		SO4-S (ppm)		Total S (ppm)		SO4-S (kg/ha)			Total S (kg/ha)		
		May	Oct.	May	Oct.	May	Oct.	May	Oct.	Incr.	May	Oct.	Incr.
Steepbank #2	lichen	4.46a	4.38b	22.6a	38.7b	447.0a	721.7b	0.7	1.2	0.5	13.4	21.6	8.2
	LFH	4.26a	4.25a	14.3a	28.8b	160.5a	226.0b	11.6	23.3	11.7	129.7	182.6	52.9
	Ae	4.86a	4.88a	2.7a	2.9a	7.3a	7.3a	3.9	4.2	0.3	10.6	10.6	0.0
	Total									12.5			61.1
Muskeg Mountain	lichen	4.49a	4.44a	23.1a	30.1b	430.0a	574.0b	0.7	0.9	0.2	12.9	17.2	4.3
	LFH	4.02a	4.00a	14.5a	20.7b	181.1a	190.0a	11.7	16.7	5.0	146.3	153.5	7.2
	Ae	4.59a	4.58a	2.4a	2.5a	7.8a	8.0a	3.5	3.6	0.1	11.3	11.6	0.3
	Total									5.3			11.8
Algar	lichen	4.43a	4.40a	25.2a	31.6b	439.9a	480.0b	0.7	0.9	0.2	13.2	14.4	1.2
	LFH	4.10a	4.08a	14.5a	13.2a	162.5a	150.0a	11.8	10.7	-1.1	131.3	121.2	-10.1
	Ae	4.62a	4.60a	2.0a	2.5a	6.0a	6.0a	2.9	3.6	0.7	8.7	8.7	0.0
	Total									-0.2			- 8.9
May	lichen	4.43a	4.43a	23.0a	24.1a	421.0a	460.0b	0.7	0.7	0.0	12.6	13.8	1.2
	LFH	4.14a	4.16a	14.0a	14.0a	196.0a	200.0a	11.3	11.3	0.0	158.3	161.6	3.3
	Ae	5.49a	5.50a	2.0a	2.0a	6.3a	6.5a	2.9	2.9	0.0	9.1	9.4	0.3
	Total									0.0			4.8

Incr.= Increase over the summer period (May to October).

For any row of pH, SO4-S or total S, values are significantly different if followed by different letter.

lichen-covered soil was separated into the lichen, LFH and Ae layers for determination of pH, soluble sulphur and total sulphur (Table 20). The two exposed sites (Steepbank #2 and Muskeg Mountain) showed a general depression in soil pH in both the lichen and LFH layer. At Steepbank #2, soil pH had been significantly lowered by nearly 0.1 unit in the lichen layer after the exposure period. Muskeg Mountain which was farther away from the emission source also showed a slight pH depression in the top layers of the soil. At the control site (May), soil pH had apparently remained constant from the start to the end of the experimental period. The Algar site also showed a slight soil pH depression, but the variability among replicates was too large and the pH depression was insignificant statistically.

4.3.1.2 Soluble sulphur and total sulphur gained by lichen and soil exposed to SO2 emissions

Sulphur in the form of sulphate is available to plants. It is a standard method of analyzing soils to determine the amount of crop-available sulphur. However, in this work soluble sulphate only represented part of the sulphur absorbed by soil and some of the absorbed sulphur was apparently found in the non-extractable form.

After exposure to SO2 emissions for six months, the lichen-covered soil was separated into three layers for sulphate-sulphur and total sulphur determinations. The results (Table 20) indicate a small increase in

sulphate-sulphur in the lichen layer. There was an increase of 0.5 Kg of sulphate-sulphur per ha, or less, in the exposed and control sites. There was a larger increase in sulphate-sulphur in the LFH layer. Steepbank #2 which was only 4 Km away from SO2 emission source gained more than 10 KgS/ha in the six months of SO2 exposure and Muskeg Mountain which was 38 Km away from SO2 emission source had gained 5 KgS/ha. The control sites showed a fairly constant sulphate-sulphur content during the experimental period. The lower depth (Ae horizon) showed little effect of SO2 emissions and there was only a small increase of sulphate-sulphur even in the exposed sites.

Much of the sulphur absorbed was not extractable by 0.1M CaCl2. The results showed that there was about 4 to 5 times as much sulphur gained in total sulphur than soluble sulphur in the Steepbank #2 site. Although the control site (May) showed no change in sulphate-sulphur content, it had actually gained 4.3 kg/ha of total sulphur in the six months of SO2 exposure. Apparently, most of the absorbed SO2 sulphur was converted to non-extractable form. Ghiorse and Alexander (1976) also found that about one quarter of the SO2 absorbed by soil was converted to non-extractable forms. Freney _et_ _al_. (1971) showed that when 10 ppm of sulphate-sulphur was added to a soil, as much as 50% of the added sulphur was incorporated into organic matter over a period of 24 weeks. Much of the work has been done on the nature of sulphur incorporated into the organic matter as a

result of the addition of fertilizer sulphur or addition of tagged sulphur. Most of the sulphur was found in the high molecular weight humic acid fraction (Freney _et al_., 1969). However, the nature of sulphur in the organic fraction as a result of SO2 absorption by soil is little known.

The author concluded that when SO2 was absorbed by soils, much of it could be immobilized and tied up in the organic fraction of soil. Only a small portion of the sulphur absorbed was found in the soluble form. Determinination of soluble sulphur content alone does not allow determination of the fate of total SO2 absorption by soil. The nature of the SO2-sulphur in the non-extractable form has yet to be investigated.

4.3.2 Sulphur Uptake by Lichen-covered Soil (Controlled Atmosphere Experiment)

Soils are capable of absorbing substantial amounts of SO2, as has been discussed in the literature review. This experiment demonstrates the capacity of soils to absorb SO2, and its effects on soil pH and soil sulphur content in a controlled atmosphere environment.

In Alberta, the maximum acceptable ground level concentration standards for SO2 in forested areas are as follows: (Anon., 1970)

a. 0.30 ppm for 30 minutes

b. 1.0 ppm for less than one hour for a short period of emergency flaring

The ambient air quality standards for Alberta in forested areas are as follows:

a. 0.30 ppm for one hour

b. 0.10 ppm for 24 hours

In this experiment, 0.10 ppm SO2 was used which resembled a reasonable concentration of SO2 found in SO2 exposed areas.

Soil covered with an intact lichen was placed in plastic open containers which had an exposed area of 95 cm^2 and volume of 3,420 cm^3. The containers were exposed to 0.10 ppm, or 100 ppb, of SO2 for seven days at either 20% or 80%

relative humidity. Lichen and soil were at field capacity moisture level when exposed to SO2. At the end of the exposure period, the samples were separated into lichen and mineral soil for determination of pH, sulphate-sulphur and total sulphur. Results (Table 21) indicate that both lichen and soil had gained a substantial amount of sulphur and at the same time pH was depressed.

4.3.2.1 The effects of 100 ppb SO2 exposure at 20% and 80% relative humidity on soil pH for seven days

After exposure to 100 ppb SO2 at 20% and 80% R.H. for seven days in the SO2 chamber, there was a slight drop in pH of both lichen and soil suggesting that the SO2 absorbed was acid forming. The pH of the lichen was found to decrease more at 80% R.H. than at 20% R.H. indicating that more SO2 had been absorbed by lichen at a higher humidity level. The mineral soil, however, did not show the same response even though soil pH had dropped after exposure at the two humidity levels. It has been shown by Smith *et al*. (1973) that when soil was moistened, more SO2 would be absorbed. The higher water content in the soil probably increased the solubility of SO2. In this experiment, the moisture in the air was raised instead which probably did not have the same effect as moistening the soil by adding water to it.

Table 21. pH values and sulphur content of a lichen-covered sandy soil exposed to 0.1 ppm sulphur dioxide for seven days under controlled conditions[1].

	pH			SO4-S (ppm)			Total S (ppm)		SO4-S (kg/ha)			Total S (kg/ha)		
	control	exposed		control	exposed		control	exposed	control	exposed	Incr.[2]	control	exposed	Incr.
							80% RH							
Lichen Layer	4.13	3.97	-0.16	6.0	40.4	34.4	680.5	790.5	0.2	1.2	1.0	31.1	36.1	5.0
Top 2.5 cm Soil	4.68	4.65	-0.03	3.4	5.3	0.9	58.3	63.5	3.6	5.7	2.1	95.0	103.5	8.5
Total														13.5
							20% RH							
Lichen Layer	4.11	4.08	-0.03	3.2	16.3	13.1	570.0	648.0	0.2	0.8	0.6	26.1	29.6	3.5
Top 2.5 cm Soil	4.74	4.52	-0.22	1.6	2.5	0.9	55.0	62.0	2.6	4.1	1.5	89.7	101.1	11.4
Total														4.9

[1] Air temperature = 22°C.
Average SO2 concentration = 100 ppb.

[2] Increase over the exposure period.

4.3.2.2 Soluble sulphate and total sulphur increase in lichen and soil after exposure to 100 ppb SO2 for seven days

After exposure to 100 ppb SO2 in the chamber for seven days, there was 1.0 to 3.0 kg/ha increase in the sulphate-sulphur content of the lichen layer and top 2.5 cm of mineral soil (Table 21). A larger amount of sulphate-sulphur was found in the lichen and mineral soil at the higher humidity level (3.1 kgS/ha at 80% R.H. and 2.1 KgS/ha at 20% R.H.). Smith et al. (1973) also showed that moist soil (50% WHC) absorbed more SO2 (9.3 to 66.8 mg per gm of air dry soil) than air dry soil (1.1 to 15.3 mg SO2 per gm of soil).

The results (Table 21) indicate a larger increase in total sulphur (5.0 to 13.0 kg/ha) than soluble sulphur at both humidity levels. The same reaction also occurred in the field experiment. Much of the sulphur was found in the non-extractable form. Soluble sulphate-sulphur analyses alone was not sufficient to determine the amount and fate of the absorbed SO2 because there were usually substantial increases in the total sulphur content of soil and yet there were only slight increases in the sulphate-sulphate content.

The results of this controlled atmosphere experiment show that SO2 was absorbed when air was relatively dry or moist. Moist air, however, increased SO2 absorption by both lichen and soil. As a result, pH of lichen and soil tended

to decrease accompanied by small increase in sulphate-sulphur and about four times as much increase in total sulphur of both lichen and soil. Soil also had a greater capability to absorb more SO2 than lichen.

The time of exposure to SO2 might be too short but the experiment was useful in determining the rate and the fate of SO2 uptake by lichen and soil.

4.4 Wet Deposition

Wet deposition refers to the process by which sulphur is brought down to earth by rain, snow and intercepted rain by vegetation.

Acid rain has been reported in northwestern Europe (Lickens, *et al.*, 1972), eastern Canada and the northeastern U.S.A. (Johnson, 1972). In Alberta, rain and snow are seldom acidic. Rainfall contributes, at the most, 4 kgS/ha/yr near SO2 emission sources and only 1 kgS/ha/yr in remote areas. However, rain intercepted by vegetation exposed to SO2 emissions could have sulphur contents 3 to 4 times greater than rain and pH as low as 3.5 (Nyborg *et al.*, 1977).

Rainfall was collected during the first week of each month from May through September, 1977 (Appendix Table 24) at the three experimental plots. Rain samples were analyzed for pH, soluble sulphur (Appendix Table 25) and total sulphur brought down by rain (Appendix Table 26).

4.4.1 pH and Soluble Sulphur Content of Rain Near SO2 Emission Source

The pH of rain determined from May to September at the three experimental plots was slightly acidic (Table 22) with only a few occasions when pH of rain was under 5.0. The lowest mean pH recorded was 5.4 at the Thickwood Hills site. The three locations were not situated downwind from the SO2 emission source, even though the AOSERP camp site was only 11 km away. The pH of rain measured in Central Alberta in the summer months of 1975 averaged 6.5 near gas processing plants, showing straight rain was not acidic (Nyborg *et al.*, 1977). Acid rain has been reported in eastern Canada but as far as western Canada is concerned, pH of rain has not come to the stage of endangering the environment.

On the average, soluble sulphur concentration was about 0.2 to 0.4 ppm recorded at the three locations. A total of about one kg/ha of sulphur was deposited onto the three forest soils from May to September. This is a small amount of sulphur deposited compared to direct SO2 absorption by soils. The total annual deposition of sulphate-sulphur in western Central Alberta was estimated to be 2.2 to 4.4 kg/ha by Walker (1969). The amount of sulphur contributed by straight rainfall is small and according to calaulation, the amount of free acidity contributed by the deposited sulphur in the rain samples was only 0.001 kgS/ha or less. Rain intercepted by vegetation could contribute as much as 3 to 4 times of sulphur. Parker (1978) found that in a pine forest

Table 22. The average pH, average soluble sulphur concentration (ppm) and total amount of sulphur (kg/ha) deposited by rain from May to September, 1977 at the three experimental sites.

Site	pH	SO4-S (ppm)	Total amount of S (kg/ha)
AOSERP Camp	5.59	0.32	0.75
Ruth Lake	6.05	0.44	1.12
Thickwood Hills	5.41	0.23	0.66

exposed to SO2 emissions, there was approximately 1.5 kg/ha of sulphur as free acidity in the combination of throughfall and stemflow.

Sulphur deposition in winter time could be much less than summer. When the ground is covered by snow, there will be less SO2 absorption by soil. Summers and Hitchon (1973) in their sulphur deposition study estimated that up to 46% of the total sulphur was deposited by rain alone within a radius of 25 miles of a emission source during summer months and no more than 2% was deposited in the same area during winter months. SO2 emitted during winter could travel a longer distance, perhaps into neighbouring provinces before it is deposited.

4.5 Effects of Increased Substrate Acidity on Moss Growth

SO2 and plant response has been studied extensively. The green plant itself functions as a monitoring device and serves as an indicator of the state of health of forests surrounding gas plants (Loman *et al*., 1972). Plant species show a wide range of sensitivity to atmospheric SO2. Among the most sensitive species are mosses and lichens (Leblanc *et al*., 1972). In the AOSERP study area, the ground is covered mostly by mosses and lichens.

The greenhouse experiment was not concerned with injury of mosses by SO2 but the effects of increased substrate acidity on moss growth. Diluted sulphuric acid was added to acidify the growing medium to various pH levels to determine

the extent to which the growth of mosses was affected by acidity. It was found that the four mosses studied showed symptoms of injury when the pH of the growing medium was below 3.5. The four mosses used in this experiment were: 1. _Hylocomium splendens_, 2. _Pleurocium scherberi_, 3. _Ptilium crista-castrensis_, and 4. _Polytrichum strictum_. Their chemical and physical properties are given in Appendix Table 27. Each moss species was cut into layers 5 cm thick and placed on a 10 cm thick layer of vermiculite in plastic pans. The pH of the substrate (vermiculite) was adjusted to 4.5, 4.0, 3.5, and 2.5. The pH was maintained by additions of acid to the side of the pans every other day for a period of 45 days.

As the experiment progressed, signs of damages to the leaf tissues were observed. When the pH of the substrate was acidified to 2.5, all four mosses were killed. At pH 3.5, leaf tissues of the mosses began to turn light brown with a gradual accumulation of a white salt on the moss leaves. This was particularly evident at the lower pH treatments after about two weeks of treatment. X-ray diffraction and sulphate-sulphur analyses showed that the salt contained a mixture of sulphate salts. The composition of the salt was not studied in detail.

The reasons for the salt deposition could be:

1. an exchange of hydrogen ions from the applied sulphuric acid with calcium and magnesium ions from the moss.
2. all mosses studied except _P. strictum_ transport their

nutrients externally by capillary action. As the calcium and magnesium salts were evaporated, they were deposited on the surface.

4.5.1 Buffering Capacity of Mosses

Mosses have high buffering ability. This was evident by the development of buffer curves (Figure 8). Buffer curves for the four mosses were developed by shaking a known volume of each moss in 100 ml of sulphuric acid of different normalities. The moss samples were left to equilibrate at each pH level for seven days and then the pH of the solution was measured.

All buffer curves showed the same general shape. The pH of the mosses dropped initially with the addition of acid and the curves leveled off with more acid added. Each moss has its own buffering capacity. Of the four mosses tested, P. strictum seemed to be most sensitive to acidity. About 3 KgS/ha as H2SO4 was enough to lower its pH by one unit. H. splendens, the most acid tolerant of the four mosses would lower its pH by one unit with the addition of less than 20 KgS/ha as H2SO4.

The four mosses studied are naturally acidic (pH 4.5 to 5.5). The soils on which they grow on are also acidic (pH 5.0 to 6.0). Further lowering of soil pH by continuous SO2 emissions could be critical to the growth of forest ground cover. According to the results of this experiment, mosses will not grow well if soil pH is below 3.5. The four mosses

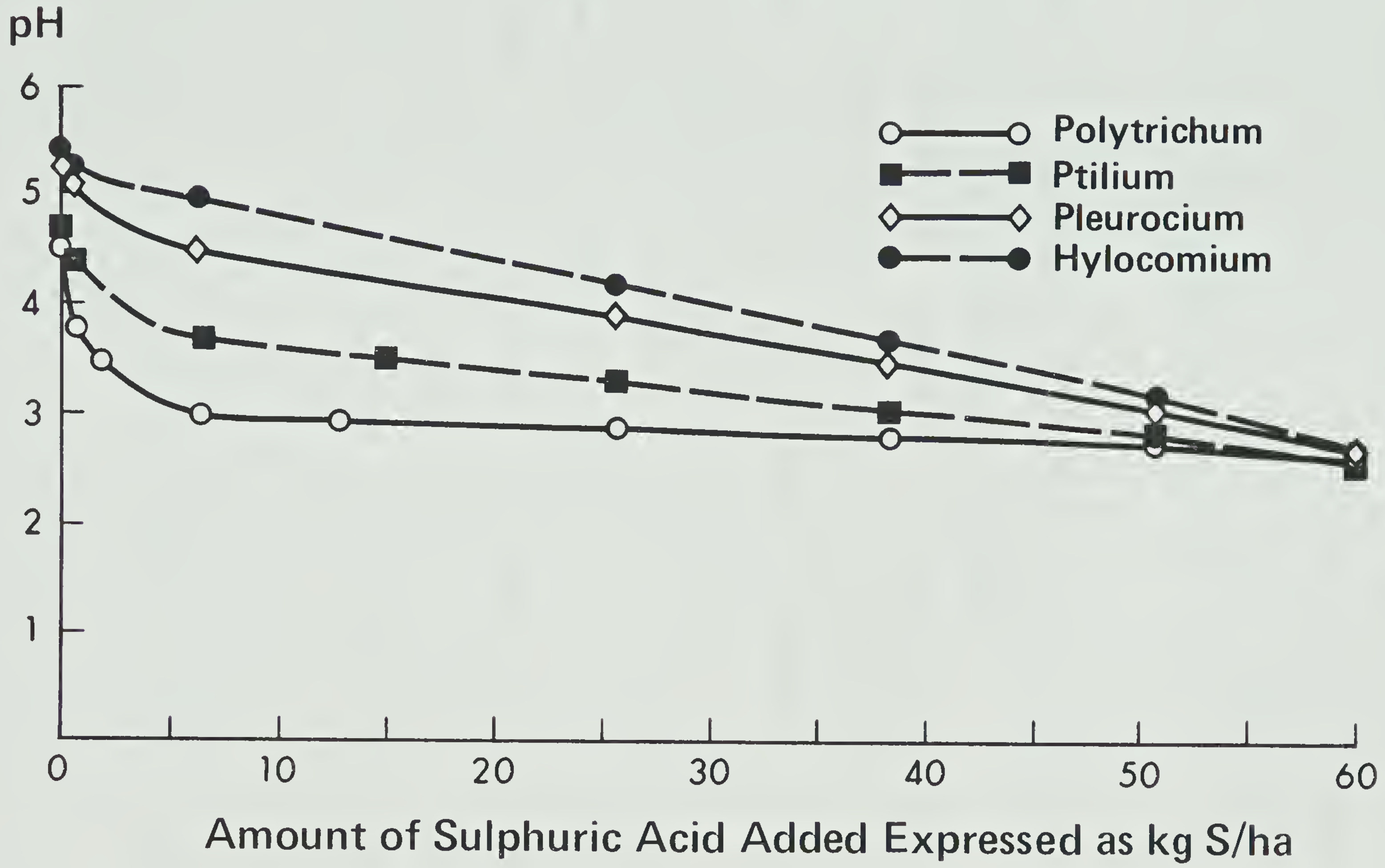


Fig. 8 Buffer curves of four mosses from the oil sands area.

studied have various buffering capacity to the change in substrate pH. It took from a few kg of sulphur to over 50 kg of sulphur to bring the moss pH below 3.5. Therefore, different species have different ability to withstand the change in pH. The gradual disappearance of mosses due to lowering of soil pH would be a good indicator of the conditions of the environment they are in.

4.5.2 Effects of Increased Substrate Acidity on the Regeneration of *Aulocomium palustra*

Mosses reproduce sexually or asexually. Every living cell of the leafy moss plant is an independent unit, and under ideal conditions each cell is capable of producing rhizoids and secondary protonemata which may give rise to buds and eventually new shoots. Thus a single moss plant can produce numerous new shoots. Clusters of brood bodies* of *A. Palustra* were used to predict the change of germination on an acidified medium. This would probably apply to some other plant species when the soil is acidified by SO2 emissions. Germination is definitely affected by pH. Therefore, by varying the pH of the substratum where these brood bodies are to germinate, one can predict how the future population of mosses will be affected.

Plastic petri dishes containing 10 ml of complete

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*Brood bodies are specialized cells produced by stems or leaves which are easily detached and propagate the plants. They can be in many forms but their main function is to reproduce the parent plant by producing protonemata.

nutrient solution (Hoagland's solution #1) were adjusted to pH 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 by the additions of various amounts of 0.1N H_2SO_4.

The control treatment which contained the nutrient solution had a pH of 5.6. Using clean forceps, a stem bearing brood bodies was transferred into the nutrient solution. (Flaming of the forceps decreased the number of bacteria or fungi which might affect germination). The petri dishes were then covered and incubated at 22°C for two weeks. The per cent germination of the brood bodies was then calculated for each treatment (Table 23).

Germination was definitely affected by low pH. Results (Table 23) indicate that pH 4.5 was the borderline between good (80%) and poor (50%) germination. There was no germination at pH 3.0 or lower. In a natural environment, one could expect a diminishing moss population at pH levels below 4.5.

Table 23. Germination of *Aulocomium palustra* brood bodies at different acid levels.

pH	% Germination of Brood Bodies
5.6 (control)	70.0
5.0	80.0
4.5	80.0
4.0	50.0
3.5	10.0
3.0	0.0
2.5	0.0

5. SUMMARY AND CONCLUSIONS

In recent years, there has been a growing interest in sulphur pollution by anthropogenic emissions of sulphur oxides and other acid-forming pollutants as a result of increasing energy consumption. One of these atmospheric pollutants is SO2, and this study is devoted to SO2 in its behavior in soils. A lichen-covered soil collected from a relatively SO2-clean area, was exposed to an SO2 emission source in the Athabasca Oil Sands area for a few summer months to determine the uptake of SO2 and soil acidification. Samples of a similar soil were also exposed to a controlled atmosphere environment in the laboratory to show the capability of soil to absorb substantial amounts of SO2. The two experiments showed the same kind of results, SO2 was absorbed by soil, and pH tended to decrease accompanied by a small increase in soluble sulphate-sulphur content. Total sulphur determination indicated that most of the sulphur absorbed was not extractable by 0.1M CaCl2, a routine analyses for crop-available sulphur. More detailed research is, therefore, required to determine the complete fate of SO2 absorption in soil and the nature of the non-extractable sulphur. The soil samples exposed near the SO2 emission source in the field gained 5 to 12 kg/ha of soluble sulphur and 2 to 5 times as much total sulphur in five months, and at the same time the pH decreased slightly for lichen-covered soil. The chemistry of the soil is

unlikey to change too drastically because of continuous SO2 emission, but soil pH would tend to lower with time.

Acid rain has been a concern in heavily industrialized areas in other countries due to the distance which SO2 can travel. In Alberta, rain and snow are seldom acidic and will contribute little or no environmental hazard. A small amount of sulphur was found in rain water collected during the experimental period. The pH of rain showed that it was only slightly acidic, seldom below 5.0. Rain intercepted by trees could contribute a larger amount of sulphur than straight rain, but SO2 absorption by soil remains to be the most important way by which SO2 is deposited in Alberta when soils are not frozen or covered by snow.

The downward movement of sulphate-sulphur was obvious after application of K2SO4 on forest soils. Sulphate-sulphur moved readily within a few wet summer months carrying with it cations particularly calcium. Total sulphur content of the soils was found to increase as a portion of the sulphate-sulphur moved downward, suggesting that some sulphur remained in the soil profile, and was not completely leached out as sulphate.

Elemental sulphur was applied onto forest soils to simulate the conditions of windblown elemental sulphur occurring near sulphur stock-piles normally found in sour gas or oil sand processing plants. Elemental sulphur caused soil acidification mainly in the upper layers of soil, but the acid can move as deep as 60 cm in twelve months in a

sandy profile. Sulphuric acid caused soil acidification as deep as 90 cm. Top dressing of lime was effective in neutralizing soil acidity, and perhaps in correcting the slow acidification process by SO2 emission. However, due to its slow diffusion downward, the effectivenss of lime was limited to the top few centimeters of the soil surface during the twelve months of experimental period.

This thesis has shown that little sulphur came down in rain and almost none of it was acidic, nevertheless, soil set out in the field gained as much as 50 times of sulphur. However, results of the three field plots suggested that any absorption of SO2 which caused soil acidification might not be easily detected because (1) the acidity may penetrate deeply into soil profiles, (2) the conversion of SO2 to acidity may be slow and (3) the absorbed sulphur is not recovered as the soluble form.

The major source of SO2 emission is the burning of fossil fuels rich in sulphur, the smelting of sulphur ores, as well as oil and natural gas processing. SO2 emission can be reduced by reducing fuel consumption and also by reduction of sulphur dioxide from fuels but it will be costly. The use of coal as a power source will also increase as oil becomes more expensive. Low sulphur coal can be used to generate power, but it is less available and more expensive than high-sulphur coal. With the current increase in oil and coal production due to energy demand, the problem of air pollution is likely to intensify unless appropriate

control measures are taken. We simply cannot produce energy without producing waste substances which could pollute the environment. As long as energy is increasingly in demand, more airborne pollutants will be produced.

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LIST OF APPENDIX TABLES

Table 1. Soil profile descriptions at the AOSERP Camp site.

Location:	11 km NW of G.C.O.S. plant developed on aeolian sand.
Vegetation:	Jack pine (Pinus banksiana) is the major of tree species with a nearly continuous lichen (Cladina mitis and C. arbuscula) ground cover.
Drainage:	Well drained.
Soil subgroup:	Eluviated Dystric Brunisol

Horizon	Description
F-H	0.5 - 0 cm; brownish black (10 YR 3/1)d semi-decomposed organic matter.
Ahe	0 - 1.5 cm; brown (10 YR 4/4)d sand; single grain; loose, friable; abundant roots; indistinct boundary.
AB	1.5 - 8 cm; dull yellowish brown (10 YR 5/4)d sand; single grain; loose, friable; abundant roots; indistinct boundary.
Bm	8 - 65 cm; yellowish brown (10 YR 5/6)d sand; single grain; loose, friable; few roots; indistinct boundary.
BC	65 - 80cm; brownish yellow (10 YR 6/6)d sand; single grain; loose, friable; no roots; transitional to C-horizon.
C	80+ cm; yellow orange (10 YR 7/8)d loose sand; single grain; loose friable; occasional stones; non-calcareous.

Table 2. Soil profile descriptions at the Ruth Lake site.

Location:	6 km south of the G.C.O.S. plant developed on aeolian sand.
Vegetation:	Jack pine (*Pinus banksiana*) is the dominant tree species; low shrubs are leather leaf (*Chamaedaphne calyculata*) and bog rosemary (*Andromeda polifolia*); the bryophyte stratum consists mainly of *Polytrichum strictum*.
Drainage:	Well drained with seasonal high water table or ground water discharge.
Soil subgroup:	Gleyed Degraded Dystric Brunisol

Horizon	Description
L-H	2.0 - 0 cm; brownish black (10 YR 3/1)d organic matter with partially decomposed coniferous leaves and mosses.
Ae	0 - 4.5 cm; light grey (10 YR 8/1)d sand; single grain; loose, friable; abundant roots; indistinct boundary.
Bm	4.5 - 25 cm; bright yellowish brown (10 YR 6/6)d sand; single grain; loose, friable; some roots; some stones and pebbles; diffuse boundary; yellowish brown mottles.
Cg	25+ cm; bright yellowish brown (10 YR 7/6)d sand; single grain; loose, friable; some stones and pebbles; yellowish brown mottles.

Table 3. Soil profile descriptions at the Thickwood Hills site.

Location:	27 km southwest of the G.C.O.S. plant developed on sandy clay loam till.
Vegetation:	The dominant tree species are trembling aspen (Populus tremuloides) with a few jack pine (Pinus banksiana) and white spruce (Picea gluca); ground is covered by scattered lichen (Cladina mitis) and mosses (Ptilium crista-castensis and Hylocomium splendens).
Drainage:	Well to imperfectly drained.
Soil subgroup:	Orthic Gray Luvisol

Horizon	Description
L-H	2 - 0 cm; black (10 YR 2/1)d organic matter of decomposed deciduous leaves and mosses.
Ae	0 - 2.5 cm; light grey (10 YR 7/1)d loam; weak fine platy; friable.
Bt	2.5 - 30 cm; dull yellowish brown (10 YR 4/3)d clay loam; medium subangular blocky, hard, firm; few roots; gradual diffuse boundary.
BCg	30 - 75 cm; dull yellowish orange (10 YR 6/3)d sandy clay loam; massive, hard, firm; few stones and pebbles; gradual diffuse boundary.

Table 4. Particle size analyses and bulk density (g/cm^3) of representative soil samples from the three sites of the movement of applied sulphur in forest soils experiment.

Sites	Depth (cm)	Sand %	Silt %	Clay %	Textural Class	Bulk Density (g/cm^3)
AOSERP Camp	0.0-2.5	93.0	2.7	4.3	S	1.28
	2.5-15	89.8	4.9	5.3	S	1.72
	15-30	91.8	2.8	5.4	S	1.96
	30-60	93.4	0.4	6.2	S	2.12
	60-90	92.0	1.7	6.3	S	2.33
Ruth Lake	0.0-2.5	89.6	3.7	6.7	S	1.50
	2.5-15	93.4	0.4	6.2	S	1.76
	15-30	90.5	1.0	8.5	S	1.97
	30-60	92.4	0.7	6.9	S	2.12
	60-90	92.1	0.6	7.3	S	2.23
Thickwood Hills	0.0-2.5	33.3	48.8	17.8	L	1.00
	2.5-15	27.6	27.2	45.2	CL	1.23
	15-30	32.0	32.6	35.4	CL	1.44
	30-60	63.5	25.2	11.3	SCL	1.55

Table 5. Analyses of representative lichen-covered soil used in determining sulphur uptake by undisturbed soils in a field experiment.

Horizon	Thickness (cm)	pH	Sand %	Silt %	Clay %	Bulk Density (g/cm^3)	Organic Matter %
Lichen	3.8	4.5	N/A[1]	N/A	N/A	0.02	N/A
LFH	0.5	4.1	N/A	N/A	N/A	0.53	15.2
Ae	8.0	4.6	51.5	37.5	11.0	0.95	3.9

[1] Not applicable.

Table 6. Analyses of representative lichen-covered soil used in determining sulphur uptake in a controlled atmosphere experiment.

Horizon	Thickness (cm)	pH	Sand %	Silt %	Clay %	Bulk Density (g/cm³)
Lichen	3.8	4.12	--	--	--	0.03
Sand	2.5	4.71	90.5	2.2	7.3	1.07

Table 7. Amount of soluble sulphur of K2SO4 experiment at the AOSERP Camp site during the experimental period (June, 1976 - June, 1977).

Treatments	Depth(cm)	SO4-S (ppm) June,76	Sept.,76	June,77
Control	2.5- 0.0	49.0a	59.0b	46.9b
	0.0- 2.5	12.0a	11.2a	10.8a
	2.5-15.0	1.7a	1.7a	0.8a
	15.0-30.0	2.6a	2.4a	0.8a
	30.0-60.0	0.9a	1.7a	0.7a
	60.0-90.0	1.7a	1.4a	0.4a
K2SO4 @ 56 KgS/ha	2.5- 0.0	58.5a	64.2b	63.4b
	0.0- 2.5	14.5a	18.4a	13.1b
	2.5-15.0	2.9a	4.5a	1.4a
	15.0-30.0	2.2a	4.5a	2.3a
	30.0-60.0	1.9a	3.7a	2.2a
	60.0-90.0	2.3a	1.7a	0.9a
K2SO4 @ 112 KgS/ha	2.5- 0.0	53.5a	83.0b	63.7c
	0.0- 2.5	8.9a	16.1b	12.7b
	2.5-15.0	2.6a	10.0b	3.0a
	15.0-30.0	2.3a	4.5a	3.5a
	30.0-60.0	1.9a	2.5a	2.3a
	60.0-90.0	2.6a	1.8a	1.6a

For any row, values are statistically different when followed by different letters. June,1976 soil sampling was made immediately before application of treatments.

Table 8. Concentration of soluble sulphur of K2SO4 experiment at the Ruth Lake site during the experimental period (June, 1976-June, 1977).

		SO4-S (ppm)		
Treatments	Depth(cm)	June,76	Sept.,76	June,77
Control	2.5- 0.0	121.5a	107.4b	79.7c
	0.0- 2.5	5.8a	8.9a	10.3a
	2.5-15.0	1.4a	1.4a	2.1a
	15.0-30.0	1.0a	1.8a	1.1a
	30.0-60.0	1.2a	2.3a	0.7a
	60.0-90.0	--	2.4a	0.8a
K2SO4 @ 56 KgS/ha	2.5- 0.0	122.4a	181.7b	79.3c
	0.0- 2.5	8.9a	16.7a	1.5a
	2.5-15.0	1.2a	8.6a	0.6a
	15.0-30.0	0.6a	3.4a	0.8a
	30.0-60.0	0.6a	3.5a	0.8a
	60.0-90.0	--	2.6a	0.8a
K2SO4 @ 112 KgS/ha	2.5- 0.0	135.8a	241.8b	86.0c
	0.0- 2.5	9.9a	21.2b	2.0a
	2.5-15.0	1.1a	5.1a	0.7a
	15.0-30.0	1.0a	11.8b	1.4a
	30.0-60.0	1.1a	7.5a	0.8a
	60.0-90.0	--	1.7a	1.0a

For any row, values are statistically significant when followed by different letters. June,1976 soil sampling was made immediately before application of treatments.

Table 9. Concentration of soluble sulphur (ppm) of K2SO4 experiment at the Thickwood Hills site during the experimental period (June, 1976 - June, 1977).

		SO4-S (ppm)		
Treatments	Depth(cm)	June,76	Sept.,76	June,77
Control	2.5- 0.0	62.6a	59.9a	56.2a
	0.0- 2.5	28.9a	27.6a	29.7a
	2.5-15.0	4.0a	4.9a	5.3a
	15.0-30.0	3.0a	4.1a	4.3a
	30.0-60.0	4.2a	3.1a	3.0a
	60.0-90.0	3.1a	3.0a	2.7a
K2SO4 @ 56 KgS/ha	2.5- 0.0	65.2a	67.8a	49.2a
	0.0- 2.5	20.2a	29.7a	31.2a
	2.5-15.0	5.1a	13.3a	5.1a
	15.0-30.0	3.1a	6.7a	4.4a
	30.0-60.0	3.5a	4.1a	2.9a
	60.0-90.0	3.6a	4.2a	3.4a
K2SO4 @ 112 KgS/ha	2.5- 0.0	69.5a	77.4a	74.8a
	0.0- 2.5	20.9a	35.0b	30.7a
	2.5-15.0	4.1a	12.7a	10.2a
	15.0-30.0	3.5a	16.7b	7.1a
	30.0-60.0	3.1a	3.8a	4.9a
	60.0-90.0	3.7a	3.3a	1.3a

For any row, values are statistically significant when followed by different letters. June,1976 soil sampling was made immediately before application of treatments.

Table 10. Soil pH of the three field plots four and twelve months after application of K2SO4 at two rates onto the surface.

		AOSERP Camp site		
Treatments	Depth(cm)	June,76*	Sept.,76	June,77
Control	2.5- 0.0	4.48a	4.28a	4.58a
	0.0- 2.5	5.39a	5.31a	5.17a
	2.5-15.0	5.70a	5.66a	5.53a
	15.0-30.0	5.64a	5.82a	5.64a
	30.0-60.0	5.81a	5.82a	5.78a
	60.0-90.0	5.79a	5.87a	5.80a
K2SO4 @ 56 KgS/ha	2.5- 0.0	4.50a	4.37a	4.71a
	0.0- 2.5	5.42a	5.39a	5.66a
	2.5-15.0	5.59a	5.68a	5.40a
	15.0-30.0	5.62a	5.70a	5.73a
	30.0-60.0	5.64a	5.74a	5.73a
	60.0-90.0	5.77a	5.70a	5.75a
K2SO4 @ 112 KgS/ha	2.5- 0.0	4.56a	4.50a	4.73a
	0.0- 2.5	5.49a	5.41a	5.37a
	2.5-15.0	5.76a	5.65a	5.52a
	15.0-30.0	5.61a	5.49a	5.53a
	30.0-60.0	5.76a	5.73a	5.69a
	60.0-90.0	5.86a	5.81a	5.87a

* Before K2SO4 was applied.

For any row at each site, values are statistically different when followed by different letters.

Table 10. Continued.

Treatments	Depth(cm)	Ruth Lake site June,76	 Sept.,76	 June,77
Control	2.5- 0.0	4.20a	4.13a	4.39a
	0.0- 2.5	4.44a	4.52a	4.54a
	2.5-15.0	4.81a	4.88a	4.85a
	15.0-30.0	5.26a	5.16a	5.07a
	30.0-60.0	5.50a	5.37a	5.20a
	60.0-90.0	--	5.51a	5.32a
K2SO4 @ 56 KgS/ha	2.5- 0.0	4.12a	4.25a	4.29a
	0.0- 2.5	4.35a	4.72a	4.73a
	2.5-15.0	4.80a	4.98a	4.91a
	15.0-30.0	5.01a	5.20a	4.93a
	30.0-60.0	5.26a	5.29a	5.13a
	60.0-90.0	--	5.57a	5.17b
K2SO4 @ 112 KgS/ha	2.5- 0.0	4.19a	4.22a	4.23a
	0.0- 2.5	4.39a	4.57a	4.58a
	2.5-15.0	4.68a	4.79a	4.79a
	15.0-30.0	5.06a	5.06a	5.05a
	30.0-60.0	5.25a	5.32a	5.20a
	60.0-90.0	--	5.59a	5.27b

For any row at each site, values are statistically different when followed by different letters.

Table 10. Continued.

Treatments	Depth(cm)	Thickwood Hills site		
		June,76	Sept.,76	June,77
Control	2.5- 0.0	5.11a	4.76a	4.94a
	0.0- 2.5	5.05a	5.03a	4.90a
	2.5-15.0	5.16a	5.30a	5.15a
	15.0-30.0	5.16a	5.34a	5.09a
	30.0-60.0	5.44a	5.49a	5.31a
	60.0-90.0	5.77a	5.76a	5.72a
K2SO4 @ 56 kgS/ha	2.5- 0.0	5.08a	4.86a	5.04a
	0.0- 2.5	5.06a	5.18a	5.37a
	2.5-15.0	5.13a	5.15a	5.28a
	15.0-30.0	5.20a	5.21a	5.22a
	30.0-60.0	5.37a	5.55a	5.42a
	60.0-90.0	5.83a	5.92a	5.90a
K2SO4 @ 112 kgS/ha	2.5- 0.0	5.11a	4.91a	4.96a
	0.0- 2.5	5.12a	5.30a	5.41a
	2.5-15.0	5.18a	5.10a	5.44a
	15.0-30.0	5.16a	5.07a	5.41a
	30.0-60.0	5.27a	5.43a	5.34a
	60.0-90.0	5.57a	5.84a	5.71a

For any row at each site, values are statistically different when followed by different letters.

Table 11. Amount of soil total S content (kg/ha) twelve months after treatments at the AOSERP Camp site (June, 1977).

		Total S (kg/ha)	
Depth(cm)	Control	K2SO4 (56 kgS/ha)	K2SO4 (112 kgS/ha)
2.5- 0.0	31.2a	31.3a	37.0b
0.0- 2.5	54.6a	62.4b	99.0c
2.5-15.0	34.1a	44.6b	68.2c
15.0-30.0	34.8a	48.6b	45.8b
30.0-60.0	38.7a	44.1a	40.9a
60.0-90.0	30.8a	31.9a	33.1a

For any row, values are statistically different when followed by different letters.

Table 12. Amount of soil total S content (kg/ha) twelve months after treatments at the Ruth Lake site (June, 1977).

Depth(cm)	Control	Total S (kg/ha) K_2SO_4 (56 kgS/ha)	K_2SO_4 (112 kgS/ha)
2.5- 0.0	53.2a	54.2a	56.6a
0.0- 2.5	80.0a	99.0b	118.9c
2.5-15.0	37.5a	53.0ab	57.7b
15.0-30.0	37.0a	40.0a	50.0a
30.0-60.0	35.0a	39.0a	41.0a
60.0-90.0	25.0a	27.0a	30.0a

For any row, values are statistically different when followed by different letters.

Table 13. Amount of soil total S content (kg/ha) twelve months after treatments at the Thickwood Hills site (June, 1977).

		Total S (kg/ha)	
Depth(cm)	Control	K2SO4 (56 kgS/ha)	K2SO4 (112 kgS/ha)
2.5- 0.0	59.8a	60.0a	65.0a
0.0- 2.5	63.0a	80.0b	107.0c
2.5-15.0	54.0a	65.0b	80.0c
15.0-30.0	46.0a	54.0b	56.0b
30.0-60.0	47.0a	53.0b	56.0b
60.0-90.0	39.0a	45.0a	44.0a

For any row, values are statistically different when followed by different letters.

Table 14. Soil pH at the AOSERP Camp site at four and twelve months after application of elemental sulphur at various rates in June, 1976.

		Soil pH		
Treatments	Depth(cm)	June,76	Sept.,76	June,77
S° @	2.5- 0.0	4.33a	4.32a	4.30a
56 kg/ha	0.0- 2.5	5.26a	4.94b	4.98b
	2.5-15.0	5.54a	5.51a	5.46a
	15.0-30.0	5.52a	5.65a	5.59a
	30.0-60.0	5.67a	5.85a	5.85a
	60.0-90.0	5.76a	*	5.90a
S° @	2.5- 0.0	4.33a	4.03b	4.00b
280 kg/ha	0.0- 2.5	5.26a	4.90b	4.77b
	2.5-15.0	5.54a	5.54a	5.20b
	15.0-30.0	5.52a	5.46a	5.34a
	30.0-60.0	5.67a	5.83a	5.62a
	60.0-90.0	5.76a	*	5.73a
S° @	2.5- 0.0	4.33a	*	3.83a
560 kg/ha	0.0- 2.5	5.26a	*	4.60b
	2.5-15.0	5.54a	*	5.44a
	15.0-30.0	5.52a	*	5.42a
	30.0-60.0	5.67a	*	5.50a
	60.0-90.0	5.76a	*	5.60a
S° @	2.5- 0.0	4.33a	5.51b	4.40a
280 kg/ha	0.0- 2.5	5.26a	5.26a	5.15a
+ lime @	2.5-15.0	5.54a	5.53a	5.50a
2500 kg/ha	15.0-30.0	5.52a	5.66a	5.57a
	30.0-60.0	5.67a	5.77a	5.69a
	60.0-90.0	5.76a	5.94a	5.81a

* no soil sampling

For any row, values are statistically significant when followed by different letters.

Table 15. Soil pH at the Ruth Lake site at four and twelve months after application of elemental sulphur, sulphuric acid and lime in June, 1976.

		Soil pH		
Treatments	Depth(cm)	June,76	Sept.,76	June,77
S° @ 280 kgS/ha	2.5- 0.0	4.04a	3.55b	4.06a
	0.0- 2.5	4.40a	3.94b	4.13c
	2.5-15.0	4.74a	4.80a	4.46a
	15.0-30.0	5.08a	5.30b	5.31b
	30.0-60.0	5.43a	5.62a	5.44a
	60.0-90.0	5.39a	*	5.42a
H2SO4 @ 280 kgS/ha	2.5- 0.0	4.04a	3.47b	3.85c
	0.0- 2.5	4.40a	3.86b	4.19c
	2.5-15.0	4.74a	4.39b	4.67a
	15.0-30.0	5.08a	4.62b	5.05a
	30.0-60.0	5.43a	5.38a	5.31a
	60.0-90.0	5.39a	5.63b	5.38a
Lime @ 2500 kg/ha	2.5- 0.0	4.04a	6.34b	6.26a
	0.0- 2.5	4.40a	5.40b	4.99c
	2.5-15.0	4.70a	5.13b	5.12b
	15.0-30.0	5.08a	5.23a	5.09a
	30.0-60.0	5.43a	5.50a	5.37a
	60.0-90.0	5.39a	5.56a	5.41a

For any row, values are statistically different when followed by different letters.

Table 16. Soil pH at the Thickwood Hills site at four and twelve months after application of elemental sulphur, sulphuric acid and lime in June, 1976.

Treatments	Depth(cm)	Soil pH June,76	 Sept.,76	 June,77
S° @ 280 kgS/ha	2.5- 0.0	4.96a	4.24b	4.35b
	0.0- 2.5	4.99a	4.81a	4.97a
	2.5-15.0	5.06a	5.05a	5.00a
	15.0-30.0	5.29a	5.34a	5.35a
	30.0-60.0	5.48a	5.69a	5.67a
	60.0-90.0	5.72a	*	5.91a
H_2SO_4 @ 280 kgS/ha	2.5- 0.0	4.96a	3.69b	3.99b
	0.0- 2.5	4.99a	4.13b	4.27b
	2.5-15.0	5.06a	4.81b	5.01b
	15.0-30.0	5.29a	4.88b	5.09b
	30.0-60.0	5.48a	5.27a	5.28a
	60.0-90.0	5.72a	5.67b	5.49a
Lime @ 2500 kg/ha	2.5- 0.0	4.96a	6.35b	6.10b
	0.0- 2.5	4.99a	5.85b	5.88b
	2.5-15.0	5.06a	5.24a	5.22a
	15.0-30.0	5.29a	5.38a	5.17a
	30.0-60.0	5.48a	5.59a	5.26a
	60.0-90.0	5.72a	5.94a	5.64a

For any row, values are statistically different when followed by different letters.

Table 17. Soluble sulphate-sulphur content of a sandy soil at the AOSERP Camp site at four and twelve months after elemental sulphur application at various rates.

		SO4-S (ppm)		
Treatments	Depth(cm)	June,76	Sept.,76	June,77
S° @ 56 kg/ha	2.5- 0.0	17.7a	58.2b	67.7c
	0.0- 2.5	11.8a	16.4a	14.0a
	2.5-15.0	2.4a	3.1a	2.0a
	15.0-30.0	2.4a	1.9a	1.9a
	30.0-60.0	1.6a	1.2a	1.0a
	60.0-90.0	2.2a	*	0.8a
S° @ 280 kg/ha	2.5- 0.0	17.7a	211.8b	108.3c
	0.0- 2.5	11.8a	32.4b	41.2c
	2.5-15.0	2.4a	3.2a	2.6a
	15.0-30.0	2.4a	2.6a	1.3a
	30.0-60.0	1.6a	2.3a	1.0a
	60.0-90.0	2.2a	*	1.3a
S° @ 560 kg/ha	2.5- 0.0	17.7a	*	144.3b
	0.0- 2.5	11.8a	*	62.3b
	2.5-15.0	2.4a	*	11.2a
	15.0-30.0	2.4a	*	2.9a
	30.0-60.0	1.6a	*	1.5a
	60.0-90.0	2.2a	*	1.1a
S° @ 280 kg/ha + lime @ 2500 kg/ha	2.5- 0.0	17.7a	182.0b	116.0c
	0.0- 2.5	11.8a	27.2b	26.6b
	2.5-15.0	2.4a	8.7a	5.2a
	15.0-30.0	2.4a	5.9a	2.0a
	30.0-60.0	1.6a	3.8a	1.7a
	60.0-90.0	2.2a	3.0a	1.2a

* no soil sampling

For any row, values are statistically different when followed by different letters.

Table 18. Elemental sulphur content at the AOSERP Camp site at four and twelve months after application at various rates.

Treatments	Depth(cm)	S° (ppm)	
		Sept.,76	June,77
S° @ 56 kg/ha	2.5- 0.0	78.0	46.0
	0.0- 2.5	10.0	7.0
	2.5-15.0	0.0	0.0
	15.0-30.0	*	*
S° @ 280 kg/ha	2.5- 0.0	485.0	200.0
	0.0- 2.5	62.0	40.0
	2.5-15.0	0.0	0.0
	15.0-30.0	*	*
S° @ 560 kg/ha	2.5- 0.0	*	625.0
	0.0- 2.5	*	105.0
	2.5-15.0	*	27.0
	15.0-30.0	*	0.0
S° @ 56 kg/ha + lime @ 2500 kg/ha	2.5- 0.0	350.0	170.0
	0.0- 2.5	51.0	34.0
	2.5-15.0	0.0	0.0
	15.0-30.0	*	*

* no soil sampling

Table 19. Soil pH at the AOSERP Camp site with sulphuric acid application at various rates from June, 1976 - June, 1977.

Treatments	Depth(cm)	June,76*	Sept.,76	June,77
56 kgS/ha	2.5- 0.0	4.33a	4.04b	4.37a
	0.0- 2.5	5.26a	4.73b	5.06a
	2.5-15.0	5.54a	5.36a	5.35a
	15.0-30.0	5.52a	5.50a	5.59a
	30.0-60.0	5.67a	5.74a	5.74a
	60.0-90.0	5.76a	5.94a	5.77a
280 kgS/ha	2.5- 0.0	4.33a	3.77b	4.14a
	0.0- 2.5	5.26a	4.29b	4.44b
	2.5-15.0	5.54a	4.98b	4.81b
	15.0-30.0	5.52a	5.21a	5.01a
	30.0-60.0	5.67a	5.57a	5.53a
	60.0-90.0	5.76a	5.77a	5.72a
560 kgS/ha	2.5- 0.0	4.33a	*	3.81b
	0.0- 2.5	5.26a	*	4.50b
	2.5-15.0	5.54a	*	4.58b
	15.0-30.0	5.52a	*	4.70b
	30.0-60.0	5.67a	*	5.00b
	60.0-90.0	5.76a	*	5.47b

* The soil was sampled immediately before the sulphuric acid was applied.

For any row at each site, values are statistically different when followed by different letters.

Table 20. Soluble sulphate-sulphur content (kg/ha) and change in soil pH at four and twelve months after the application of sulphuric acid on a sandy soil (AOSERP Camp site) at various rates.

		Sept.,1976		June,1977		pH	
Treatments	Depth(cm)	Net (ppm)	SO4-S (Kg/ha)	Net (ppm)	SO4-S (Kg/ha)	Sept. 1976	June 1977
56 kgS/ha	2.5- 0.0	24.6	1.5	4.9	0.3	-0.44	-0.35
	0.0- 2.5	11.4	22.2	5.4	10.6	-0.36	-0.08
	2.5- 15.0	1.2	3.3	2.6	6.8	-0.28	-0.31
	15.0- 30.0	1.4	4.2	2.7	8.1	-0.16	-0.07
	30.0- 60.0	0.6	2.1	1.0	3.2	-0.10	-0.07
	60.0- 90.0	0.0	0.0	0.3	1.1	0.00	-0.09
	90.0-120.0	*	*	0.6	2.1	*	-0.02
		Recovery	33.3		32.2		
280 kgS/ha	2.5- 0.0	303.2	18.5	24.6	1.5	-0.71	-0.58
	0.0- 2.5	41.2	80.3	13.4	26.2	-0.80	-0.70
	2.5- 15.0	20.1	52.6	7.3	19.1	-0.66	-0.85
	15.0- 30.0	14.0	41.8	9.4	28.1	-0.45	-0.65
	30.0- 60.0	6.3	20.3	4.6	14.8	-0.27	-0.28
	60.0- 90.0	2.8	10.0	3.3	11.8	-0.17	-0.14
	90.0-120.0	*	*	3.3	11.8	*	-0.04
		Recovery	223.5		113.3		
560 kgS/ha	2.5- 0.0	*	*	13.1	0.8	*	-0.91
	0.0- 2.5	*	*	24.6	48.0	*	-0.64
	2.5- 15.0	*	*	19.4	50.8	*	-1.08
	15.0- 30.0	*	*	21.8	65.1	*	-0.12
	30.0- 60.0	*	*	15.3	49.4	*	-0.81
	60.0- 90.0	*	*	10.6	37.7	*	-0.39
	90.0-120.0	*	*	5.8	20.7	*	-0.34
		Recovery			272.5		

* no soil samples taken

Table 21. Soluble sulphate-sulphur content (kg/ha) and change in soil pH at four and twelve months after the application of sulphuric acid on a sandy soil (Ruth Lake site) at 280 kgS/ha.

	Sept., 1976		June, 1977		pH	
Depth (cm)	Net (ppm)	SO4-S (kg/ha)	Net (ppm)	SO4-S (kg/ha)	Sept. 1976	June 1977
2.5- 0.0	143.9	13.1	8.8	0.8	-0.87	-0.59
0.0- 2.5	10.3	23.5	2.1	4.8	-0.70	-0.42
2.5- 15.0	1.3	3.4	0.3	0.9	-0.56	-0.35
15.0- 30.0	8.9	26.7	0.4	1.2	-0.63	-0.02
30.0- 60.0	4.8	15.5	3.1	10.1	-0.19	-0.06
60.0- 90.0	0.7	2.4	0.5	1.7	-0.06	-0.05
90.0-120.0	--	--	0.1	0.4	--	-0.03
Recovery		84.6		19.9		

Table 22. Soluble sulphate-sulphur content (kg/ha) and change in soil pH at four and twelve months after the application of sulphuric acid on a clay loam soil (Thickwood Hills site) at 280 kgS/ha.

	Sept.,1976		June,1977		pH	
Depth(cm)	Net (ppm)	SO4-S (Kg/ha)	Net (ppm)	SO4-S (Kg/ha)	Sept. 1976	June 1977
2.5- 0.0	131.7	3.5	14.9	-0.9	-1.06	-0.81
0.0- 2.5	24.5	21.6	4.0	-0.8	-0.94	-0.93
2.5- 15.0	31.3	53.3	7.0	9.9	-0.37	-0.19
15.0- 30.0	51.3	108.1	6.8	12.7	-0.51	-0.06
30.0- 60.0	10.2	21.0	5.5	10.2	-0.38	-0.19
60.0- 90.0	2.1	1.9	2.7	4.4	-0.29	-0.16
90.0-120.0	--	--	1.8	1.5	--	-0.25
Recovery		209.4		37.0		

Table 23. Soluble sulphate-sulphur concentrations (ppm) of a sandy soil at AOSERP Camp site with sulphuric acid application at various rates from June, 1976-June, 1977.

		SO4-S (ppm)		
Treatments	Depth(cm)	June,76**	Sept.,76	June,77
56 KgS/ha	2.5- 0.0	17.7a	45.0b	27.7c
	0.0- 2.5	11.8a	16.2b	6.7c
	2.5-15.0	2.4a	3.8a	3.5a
	15.0-30.0	2.4a	3.6a	3.4a
	30.0-60.0	1.6a	2.0a	1.8a
	60.0-90.0	2.2a	1.3a	1.1a
280 KgS/ha	2.5- 0.0	17.7a	323.0b	47.7c
	0.0- 2.5	11.8a	46.0b	14.7c
	2.5-15.0	2.4a	22.6b	8.2a
	15.0-30.0	2.4a	16.2b	10.1b
	30.0-60.0	1.6a	7.7a	5.4a
	60.0-90.0	2.2a	4.1a	4.1a
560 KgS/ha	2.5- 0.0	17.7a	*	37.0b
	0.0- 2.5	11.8a	*	25.9b
	2.5-15.0	2.4a	*	20.3b
	15.0-30.0	2.4a	*	22.5b
	30.0-60.0	1.6a	*	16.1b
	60.0-90.0	2.2a	*	11.4b

* no soil sampling

** The soil was sampled immediately before sulphuric acid was applied.

For any row, values are statistically different when followed by different letters.

Table 24. Total precipitation (mm) at the three experimental sites from May to September, 1977.

Site	Rainfall (mm)					
	May	June	July	Aug.	Sept.	Total(mm)
AOSERP Camp	42.5	83.0	35.0	48.0	35.0	243.5
Ruth Lake	75.3	69.8	44.5	38.6	45.0	273.2
Thickwood Hills	76.8	94.7	56.9	52.7	30.0	311.1

Table 25. pH and sulphur concentrations (ppm) of rain water collected montly from May to September, 1977 at the three experimental sites.

	AOSERP Camp		Ruth Lake		Thickwood Hills	
	pH	SO4-S	pH	SO4-S	pH	SO4-S
May	4.67	0.32	6.35	0.40	4.83	0.32
June	5.60	0.30	6.46	0.50	5.75	0.22
July	4.83	0.28	5.96	0.32	4.55	0.12
August	6.43	0.42	6.15	0.48	5.88	0.18
September	6.41	0.30	5.32	0.50	6.04	0.30

Table 26. Amount of sulphur (kg/ha) brought down by rain from May to September, 1977 at the three experimental sites.

Site	May	June	July	August	September	Total
AOSERP Camp	0.14	0.23	0.09	0.19	0.10	0.75
Ruth Lake	0.28	0.33	0.13	0.17	0.21	1.12
Thickwood Hills	0.23	0.20	0.06	0.09	0.08	0.66

Table 27. pH and bulk density of representative samples of the four mosses from the AOSERP study area.

Moss	pH	bulk density (g/cm^3)
Hylocomium splendens	5.4	0.14
Plaurocium scherberi	5.3	0.18
Ptilium crista-castrensis	4.7	0.20
Polytrichum strictum	4.5	0.60

LIST OF APPENDIX FIGURES

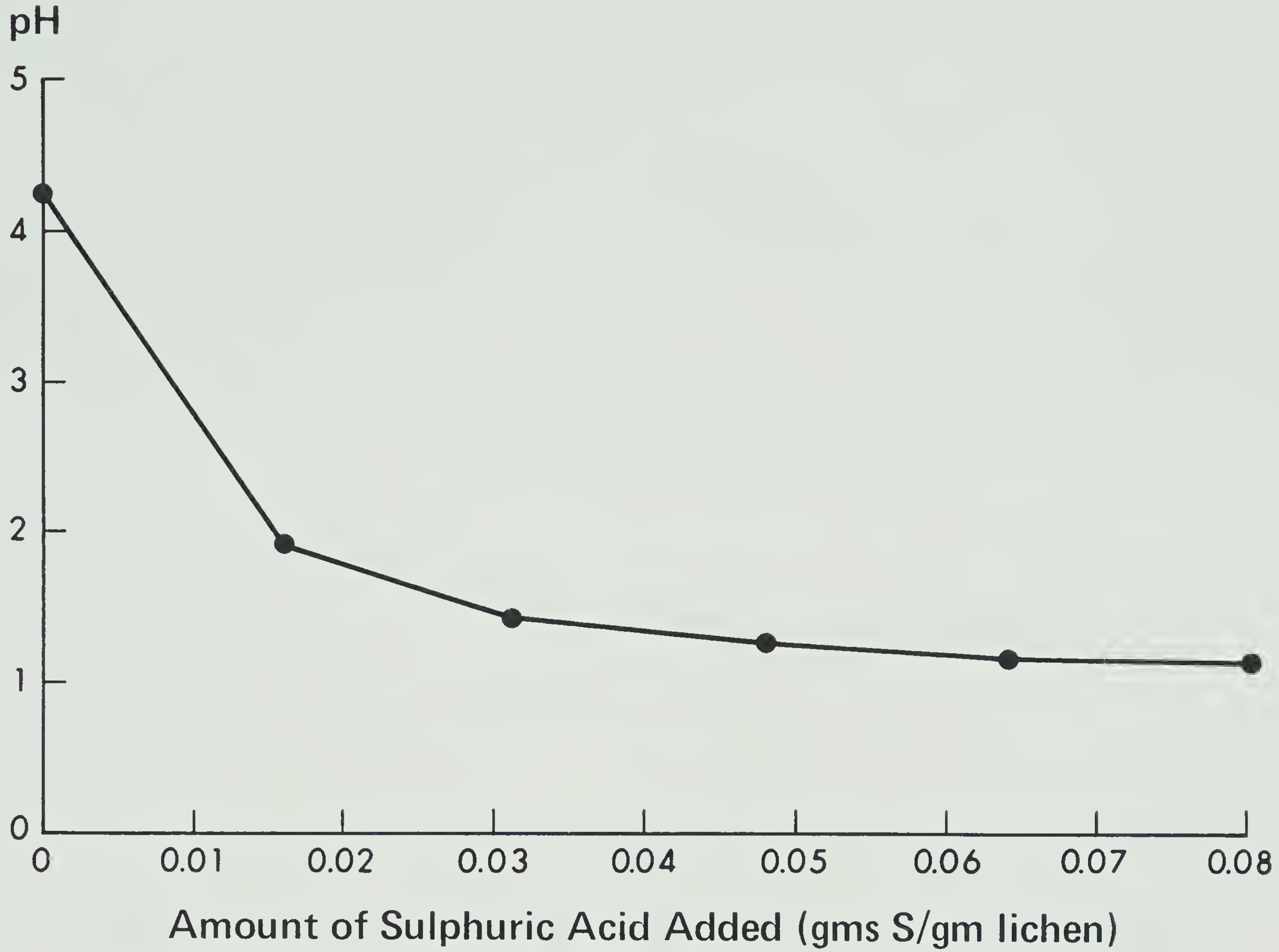

Fig. 1 Buffer curve of the lichen (*C. mitis*) from the sulphur dioxide uptake by lichen covered soils field experiment (May-September 1977). Each point was determined by the addition of various amounts of 0.1N sulphuric acid in 50 ml water. The pH was measured after an equilibrating period of 7 days.

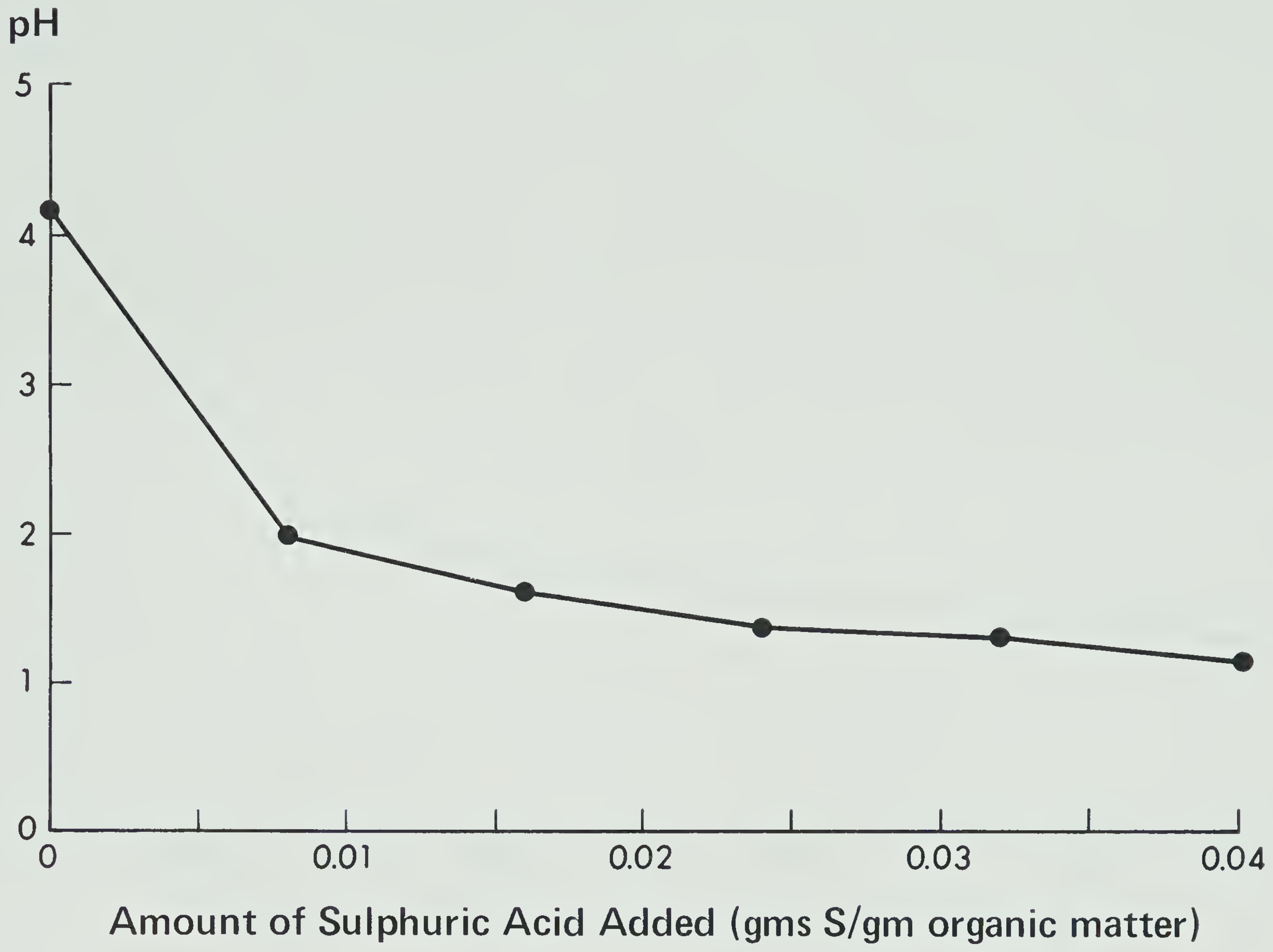

Fig. 2 Buffer curve of the LFH horizon from the sulphur dioxide uptake by lichen covered soils field experiment (May-September 1977). Each point was determined by the addition of various amounts of 0.1N sulphuric acid in 50 ml water. The pH was measured after an equilibrating period of 7 days.

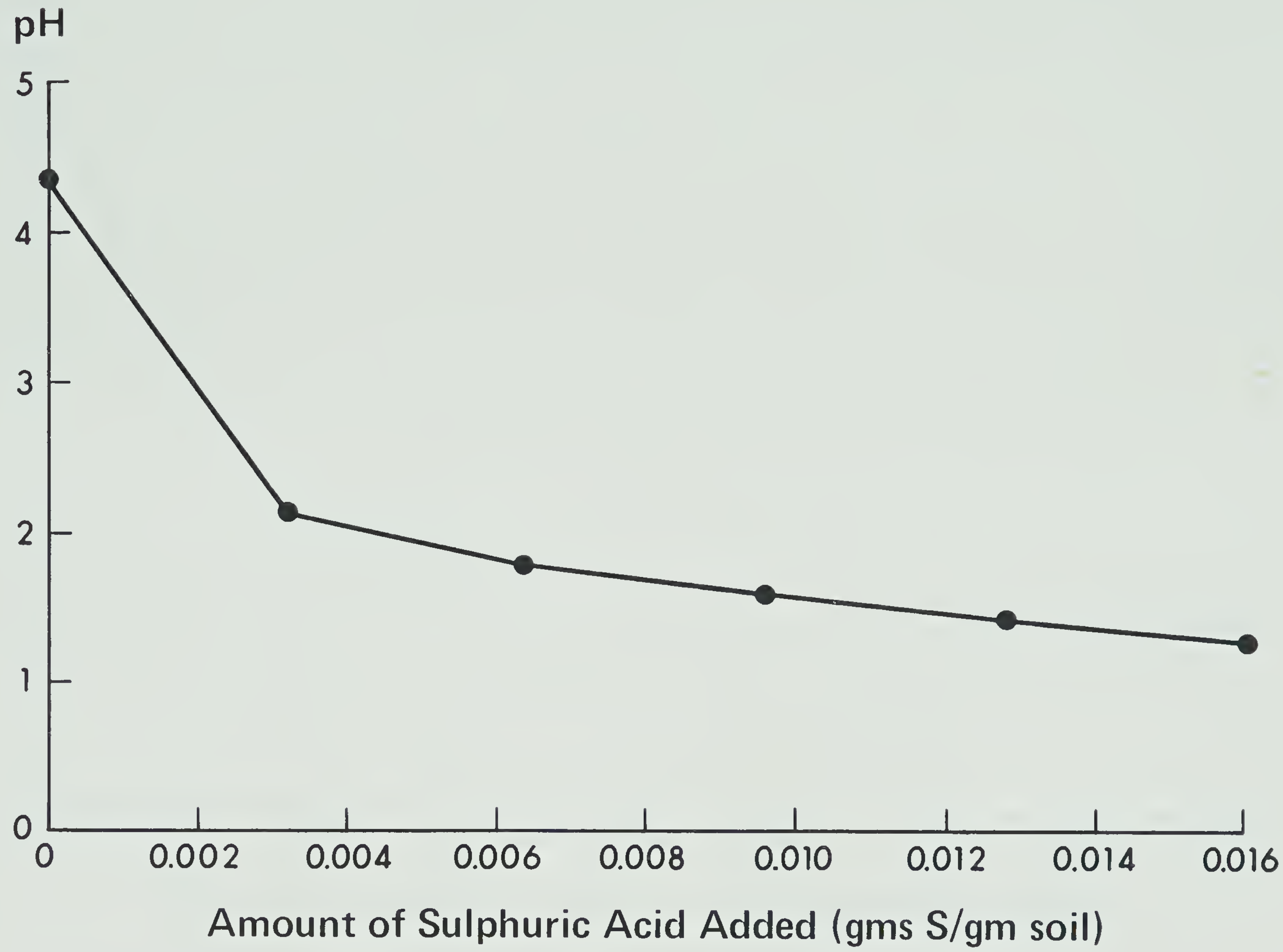

Fig. 3 Buffer curve of the Ae horizon from the sulphur dioxide uptake by lichen covered soils field experiment (May-September 1977). Each point was determined by the addition of various amounts of 0.1N sulphuric acid in 50 ml water. The pH was measured after an equilibrating period of 7 days.

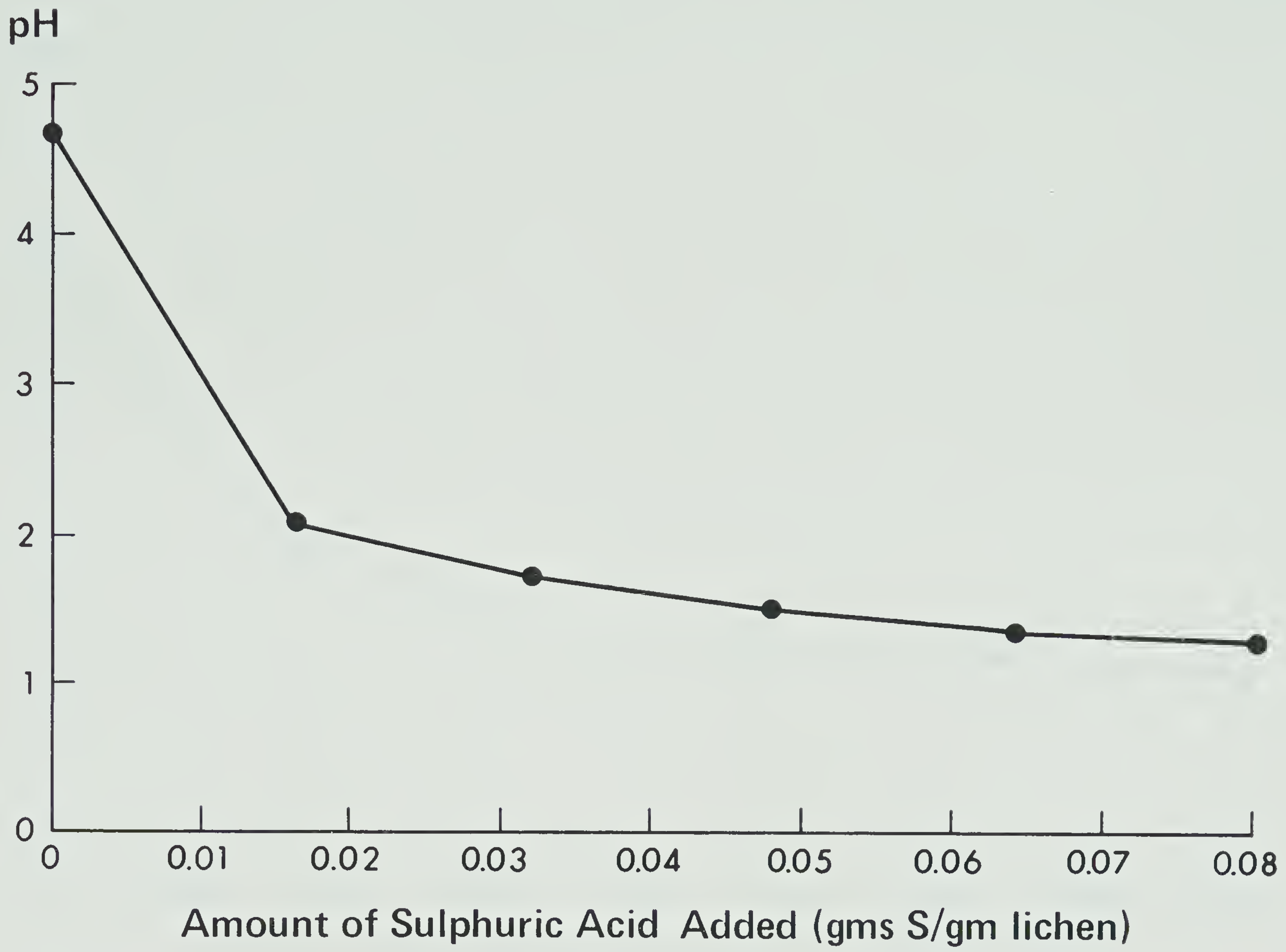

Fig. 4 Buffer curve for the lichen (*C. mitis*) used in the sulphur dioxide chamber experiment (Oct 1977). Each point was determined by the addition of various amounts of 0.1N sulphuric acid in 50 ml water. The pH was measured after an equilibrating period of 7 days.

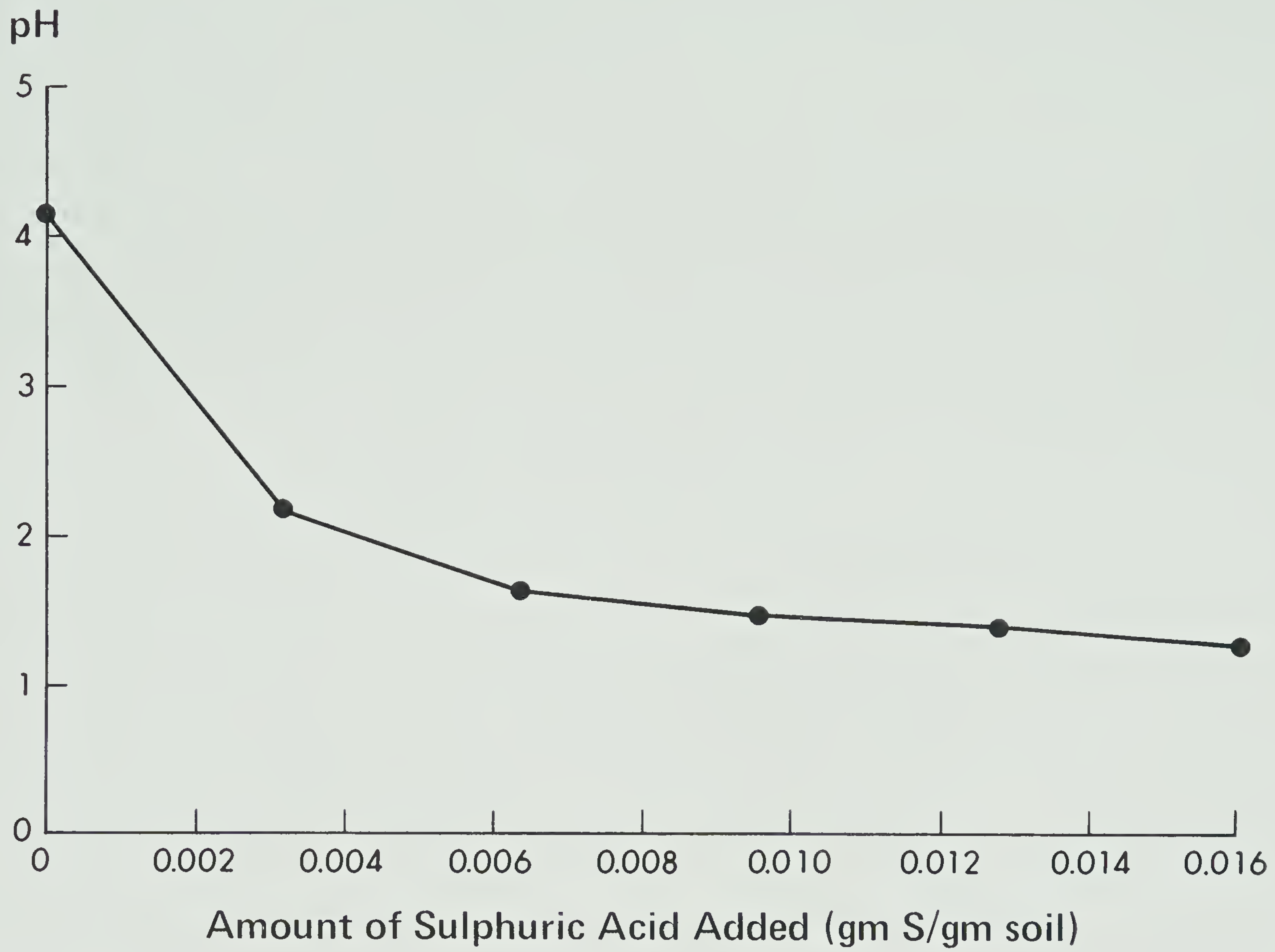

Fig. 5 Buffer curve for top 2.5 cm of soil (LFH + Ae) used in the sulphur dioxide chamber expt. (Oct 1977). Each point was determined by the addition of various amounts of 0.1N sulphuric acid in 50 ml water. The pH was measured after an equilibrating period of 7 days.

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